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THE SOLUBILITY OF THE PHOSPHATES OF CALCIUM IN AQUEOUS SOLUTIONS OF SULFUR DIOXIDE

BY W. M. MEBANE, J. T. DOBBINS AND F. K. CAMERON

Introduction

It has been known for many years that phosphate rock suspended in water is made more soluble by absorption of sulfur dioxide, and that the resulting solution contains the base and acid in a ratio differing from the ratio in the suspended solid. A number of attempts have been made to utilize these facts in the preparation of acid or "super" phosphates; particularly, for the fertilizer industry. The larger part of the plant investment in the fertilizer industry is in the lead chambers of the acid plants, and the cost of oxidizing sulfur dioxide is a dominating factor in determining the price of phosphatic fertilizers. With a lower fixed charge against a smaller plant investment and a lower manufacturing charge by eliminating the oxidation of sulfur dioxide, a cheaper fertilizer would be possible. Moreover, it should be possible to treat the raw rock "as mined" and eliminate the expensive washing process deemed necessary in the present practice, whereby fifty per cent or more of the phosphorus goes to the tailings pond.

Again, in the vicinity of some of our Western smelters are readily accessible deposits of phosphorites. The sulfur dioxide emitted in the smelting operations is a liability. The geographical position of these western phosphates lessens much their present economic importance. Both sulfur dioxide and phosphorites would become important assets if a satisfactory method of direct treatment of one by the other can be devised. There is no prospect that any significant fraction of the sulfur dioxide can ever be converted economically into sulfuric acid unless a change in metallurgical practices will afford a much richer stack gas.

Tirelli[1] claims to have made a superphosphate in the laboratory, but regards the method as inapplicable to commercial practice. Sestini[2] tried mixing chlorine with sulfur dioxide, but again the process failed practically.

The three-component system CaO-P_2O_5-H_2O was studied by Cameron and coworkers, the results with a summary of those of previous workers being brought together in a departmental bulletin[3]

Cameron and Bell[4] found that at 25 C. there is a range of high concentrations of phosphoric acid at which the stable solid phase in contact with the solutions is the mono-calcium phosphate, the solubility of the salt decreasing with increasing concentration of the acid. There is a second range of lower

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[1] Chem. Abs., **1**, 1601 (1907); Rass. Min. **26**, 101-03; 118-20.

[2] Ind. Chim., **12**, 49-53; J. Soc. Chem. Ind., **31**, 293 (1912).

[3] U. S. Department of Agriculture, Bureau of Soils, Bulletin No. 41 (1907).

[4] J. Am. Chem. Soc., **27**, 1512 (1905).

concentrations of the acid in contact with di-calcium phosphate as the stable solid phase. Finally there is a range of yet lower concentrations of phosphoric acid, in contact with a series of solid solutions, one limiting solid solution being calcium hydroxide, the other being di-calcium phosphate. No range of concentration exists at which the hypothetical tricalcium phosphate is the stable solid phase, nor is there any evidence for the existence of the tetra-calcium phosphate described by Wiley and Krug[1] and by Otto.[2]

Bassett[3] confirmed the work of Cameron and Bell, but, objecting to the concept of a series of solid solutions, postulates the probable existence of "oxy" and "hydroxy" apatites in contact with liquid solutions of low content of phosphoric acid.

Lorah, Tartar, and Wood[4] claim to have precipitated tri-calcium phosphate ($Ca_3(PO_4)_2$, by adding ammonium hydroxide to a solution of mono-calcium phosphate, at such a rate that the supernatant liquid remains continuously *very slightly* alkaline (presumably to phenol phthalein). From their own work as well as that of Bassett,[5] Kolthoff,[6] Jolibois,[7] Jolibois and Maze-Sencier,[8] and Hayashi and Matsui,[9] they concluded this precipitate selectively adsorbs calcium hydroxide from the supernatant solution. They think these adsorption complexes become, or are accompanied by the formation of, solid solutions; but, that the limiting member on the alkaline end is the hydroxy-apatite of Bassett.

Cameron and McCaughey[10] obtained chlor-apatite and chlor-spodiosite by dissolving calcium phosphates in calcium chloride, fluor-apatite by dissolving calcium fluoride in molten di-sodium phosphate, but were unable to obtain calcium tetra-phosphate. Clifford and Cameron[11] recently obtained a series of solid solutions of calcium oxide and arsenic acid in contact with dilute aqueous solutions of arsenic acid.

Gerland[12] found dicalcium phosphate to be very soluble in sulfurous acid, but was unable to isolate a definite compound from the solution. Dr. S. C. Collins[13] in a study of the vapor tensions of this system at the laboratory of the State Teachers' College, Johnson City, Tenn., has encountered this difficulty, and our own results to be presently described show that equilibrium conditions are not obtained readily when dicalcium phosphate is a solid phase in contact with solutions of sulfur dioxide. With tri-calcium phosphate

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[1] J. Anal. Chem., 5, 685 (1891).

[2] Chem. Ztg., 18, 225 (1887).

[3] Z. anal. Chem., 59, 1-55, (1908); J. Chem. Soc., 111, 620-42 (1917).

[4] J. Am. Chem. Soc., 51, 1097 (1929).

[5] J. Chem. Soc., 111, 620 (1917).

[6] Chem. Weekblad, 12, 662 (1915).

[7] Compt. rend., 169, 1161 (1919).

[8] Compt. rend., 181, 369 (1925).

[9] J. Soc. Chem. Ind., (Japan), 29, 175 (1925).

[10] J. Phys. Chem., 15, 464 (1911).

[11] Ind. Eng. Chem., 21, 69, (1929).

[12] J. prakt. Chem. (2), 4, 97 (1871)

[13] Private Communication.

Gerland obtained solutions in contact with a solid to which he ascribes the formula $Ca_3.P_2O_5.SO_2.2H_2O$. His analyses were not convincing. He must have had two solid phases, probably calcium sulfite and dicalcium phosphate[1] or a phosphate approximating it in composition.

All attempts to develop a commercial practice in this direction have proven futile. A search of the literature shows that there has not been developed the necessary scientific data on which to base such a practice.

Experiments

Preliminary trials showed that equilibrium conditions of solubility were finally obtained only after long standing with this system. It was also found that the temperature of the laboratory in which this work was done varied but little from a mean of about 26°C. Consequently the containers were not immersed in a water bath. A series of wide-mouth bottles of 500 cc. capacity each was fitted with rubber stoppers carrying appropriate inlet and outlet tubes of glass. Into each was placed about 200 ccs. of a solution of phosphoric acid, the several concentrations varying over a wide range. Appropriate solid mixtures of the phosphates of calcium and calcium carbonate were added until a solid persisted in each bottle after saturation with sulfur dioxide. This last, obtained from a commercial cylinder, was bubbled through the solutions from time to time until a stable state was obtained. The bottles containing the higher proportions of phosphoric acid were not brought to this state in less than six weeks, while those containing the lowest proportions appeared to come to equilibrium within a fortnight. With the higher concentrations of phosphoric acid, diffusion was slow, necessitating frequent shakings. There appeared to be three series of solutions. One in which there was a large excess of phosphoric acid to calcium appeared to contain but one solid phase, a clear crystalline body. At the other end where the lower ratios of phosphoric acid to calcium were obtained, there also appeared to be but one solid phase, a homogeneous, white, amorphous body. Between these two series was a third, each bottle of which appeared to contain two solids in distinct layers, the upper opaque and very finely divided, the lower transparent and fair-sized crystals. The solutions in the middle series had the straw yellow color previously noted by Gerland.

Samples of the solutions for analysis were obtained with much difficulty, due to the volatility of the sulfur dioxide. With a small pipette a sample was quickly transferred to a weighing bottle which was at once stoppered tightly and then weighed. The bottle was opened under cold water in a 600 cc. beaker, the solution further diluted to definite volume and aliquots withdrawn for analysis. As soon as possible after the dilution and mixing, the sulfur dioxide was determined by titrating with a 0.05 N solution of iodine.

Calcium was determined by adding ammonium oxalate to known excess, then adding ammonia until the solution was alkaline in reaction, and allow-

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[1] Rotondi: Annali di Chimica, 74, 128 (1882).

ing it to stand over night. During this time all calcium was precipitated as oxalate, although some of it at first came down as phosphate. The precipitate was filtered, washed, and transferred with the filter paper to a beaker, and dissolved with dilute sulfuric acid. The solution was then titrated with a 0.1N permanganate solution, the filter paper offering no difficulty if care were taken to avoid a large excess of sulfuric acid.

To determine the phosphoric acid, the aliquot was first treated with nitric acid and brought to a boil in order to expel or completely oxidize the sulfur dioxide. While yet hot, there was added about 20 times the estimated amount of a solution of ammonium molybdate. Precipitation usually started at once, but half an hour was allowed for completion. The precipitate was filtered and washed in a Gooch crucible with a solution of ammonium nitrate. It was transferred to a beaker and titrated with a 0.5 N solution of potassium hydroxide. The solution of ammonium molybdate was prepared by dissolving the salt in a concentrated solution of ammonia, and then adding nitric acid to faint acidity. To insure complete precipitation of the phosphorus a large excess of the molybdate was always used.

Identification of the solid phases presented additional difficulties to that involving loss of sulfur dioxide in sampling. Attempts to use a chlor-ion as a "tell-tale" in finding the amounts of liquid phase components adhering to the solids proved to be quite impracticable. In most cases, the liquid phase was so dense that the weight of liquid to weight of solid was too high in any sample that could be pipetted to give a chlorine percentage in the residue that would differ markedly from the percentage in the liquid phase alone. Dobbins and Gilreath[1] finding that the composition of the solid precipitated from a solution containing calcium and phosphoric acid, when an excess of ammonia is added, has approximately the proportions in the formula $Ca_3(PO_4)_2$, proposed to use the ratio of phosphoric acid precipitated to that remaining in solution as a criterion of the composition of the calcium phosphate from which the solution is made. This was used to identify the solids of the third series, but no satisfactory modification of the procedure could be devised applicable to the case where the precipitates are of necessity a mixture of two solid phases along a boundary curve, or three in contact with a constant solution. Consequently the solids were filtered as rapidly and completely as possible, dried by pressure between filter papers, and transferred to stoppered weighing bottles.

Consideration of the results obtained from the series just described made evident the desirability of finding the effect of added quantities of sulfur dioxide in the liquid phase. This end could be obtained either by increasing the pressure in the vapor phase, or, more conveniently, by absorbing the sulfur dioxide at a lower temperature. Another series of solutions and solids was prepared and saturated as before, at the temperature of an ice chest, approximating 0°C.

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[1] *Dissertation, University of North Carolina (1928).*

TABLE I

Composition of Liquid Phases in Contact with Pairs of Solids in the System: $CaO-P_2O_5-SO_2-H_2O$

25°C Isotherm

No.	Per cent CaO	Per cent P_2O_5	Per cent SO_2	Per cent H_2O	Solid Phases
1	1.92	0.00	4.57	93.51	Calcium Sulfite
2	1.27	1.30	1.60	95.83	Calcium Sulfite and Solid solution.
3	1.54	1.80	2.36	94.30	
4	1.57	1.63	2.83	93.97	"
5	1.63	1.53	2.65	94.19	"
7	2.11	3.28	1.66	92.95	"
8	2.30	3.45	1.92	92.33	"
9	2.62	4.10	2.18	91.10	"
10	2.73	4.38	2.57	90.32	"
11	3.00	3.80	4.45	88.75	"
12	3.52	4.33	6.18	85.97	"
13	4.34	5.94	7.18	82.44	"
14	4.80	6.11	4.32	84.77	"
15	5.40	6.11	2.75	85.74	"
16	5.57	5.86	4.00	84.57	"
17	6.08	7.68	2.10	84.14	Di-Calcium Phosphate and Mono-Calcium Phosphate
18	6.50	9.05	0.20	84.25	
19	5.54	9.34	1.30	83.82	"
20	5.64	9.61	1.41	83.34	"
21	5.22	10.64	1.45	82.69	"
22	4.81	10.74	1.65	82.80	"
23	5.52	11.62	0.35	82.51	"
24	5.61	11.62	1.35	81.42	"
25	6.12	11.45	0.40	82.03	"
26	6.02	11.95	0.20	81.83	"
27	6.25	16.93	2.57	74.25	"
28	6.75	18.11	2.20	72.94	"
29	6.45	21.93	0.20	71.42	"
30	6.25	22.01	0.40	71.34	"
31	5.76	27.77	0.00	66.47	Mono-Calcium Phosphate
32	5.95	28.90	0.00	65.15	"
33	6.20	29.24	0.00	64.56	"
34	5.64	33.78	0.00	60.58	"
35	5.57	36.80	0.00	57.63	"

TABLE I (Continued)

Composition of Liquid Phases in Contact with Pairs of Solids in the System: $CaO\text{-}P_2O_5\text{-}SO_2\text{-}H_2O$

0°C Isotherm

No.	Per cent CaO	Per cent P_2O_5	Per cent SO_2	Per cent H_2O	Solid Phases
36	0.03	0.00	4.03	95.94	Calcium Sulfite and
37	1.42	0.67	0.43	97.84	Solid Solution
38	1.72	1.23	1.22	95.83	"
39	2.31	1.58	2.09	94.02	"
40	2.40	1.63	2.36	93.61	"
41	2.50	1.91	2.75	92.84	"
42	4.85	3.29	7.00	84.86	"
43	4.55	6.08	7.63	81.74	Di-Calcium Phosphate and
44	6.43	13.73	2.13	77.71	Mono-Calcium Phosphate
45	6.46	13.52	1.48	78.54	

Discussion

The analytical results of the investigation of the liquid phases are assembled in Table I. Included are the results of the examination of the solid phases, given in the last column. These results are charted in Fig. 1 as the orthographic projection on the $CaO\text{-}P_2O_5\text{-}H_2O$ plane of the figure obtained by plotting the percentages of CaO, P_2O_5, SO_2, and H_2O on an equilateral tetrahedron. The crosses (x) indicate the isotherms for 25°C. The circles (o) indicate the isotherms for 0°C. At concentrations of phosphoric acid (P_2O_5) above 27.5 per cent, the sulfur dioxide content of the liquid phases is vanishingly small, and absent in the solid phases. Hence, sulfur dioxide ceases to be a component, the system becomes a three-component one, and there is but one solid phase along the boundary. The curve is not shown in the figure. The figures for sulfur dioxide content are the results of careful analysis. It is possible that equilibrium between solid and liquid phases had not been attained. It is more probable that our technique in preparing samples for analysis was inadequate. Any different method was impracticable. The results can not have any absolute value. They do, however, show the order of magnitude, and that each isotherm shows a maximum solubility for sulfur dioxide in contact with the pairs of solid phases.

Analysis of the solid phase in bottle No. 1 gives the composition represented by the formula $CaSO_3$. No other sulfite is known. Hence, it appears safe to assume that calcium sulfite is one of the solid phases in all the solids containing sulfur dioxide. This assumption made, the analyses show that the second solid phase in the series Nos. 2-16 and Nos. 36-43 is a member of a series of solid solutions, a limiting solid solution in each case being di-calcium phosphate. These conclusions are supported by the figures in Table II, in which are given the mole ratios to phosphoric acid of the lime in excess of that equivalent to sulfurous acid found to be present.

The liquid solutions in contact with solid mixtures of mono- and di-calcium phosphate appeared to come to equilibrium slowly and uncertainly. As noted above we, as other investigators, had difficulty in obtaining consistent data. Several hypotheses to account for these difficulties were investigated.

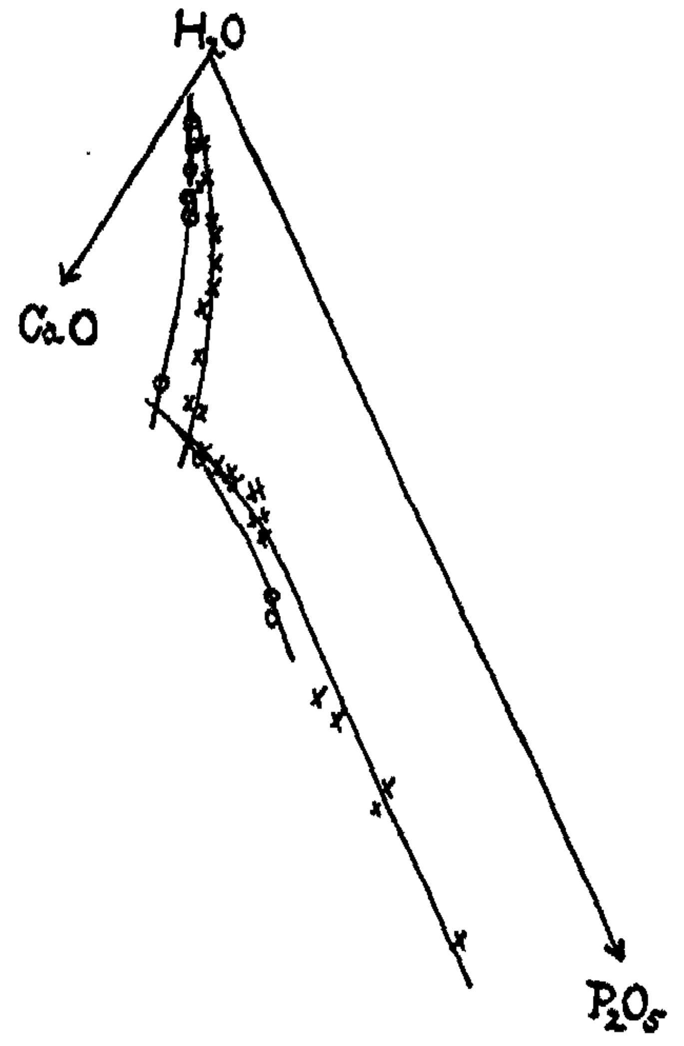

FIG. 1
Solubility isotherms for calcium phosphate in aqueous solutions of sulphur dioxide. Projection on the H_2O-CaO-P_2O_5 plane from the equilateral tetrahedron representing H_2O-CaO-P_2O_5-SO_2.

TABLE II

Ratios of Calcium Oxide to Phosphoric Anhydride in the Solid Phosphates in Contact with Aqueous Solutions saturated with Sulfur Dioxide.

Moles CaO-Moles SO_2 to Moles P_2O_5

25°C		0°C.	
Solution No.	Ratio	Solution No.	Ratio
2	6.13	37	4.90
3	4.59	38	4.72
4	4.51	39	4.41
5	4.07	40	4.33
11	3.34		
12	2.84		
21	1.98		
22	1.72		
34	1.03		

They seem to be due to the fact that in withdrawing samples for analysis sulfur dioxide escapes very readily from the sample and at the same time lime and phosphoric acid precipitate. Hence the difficulty in drawing representative liquid samples.

The isotherm for 25°C at a pressure of one atmosphere having been determined, and offering no expectation of the effective separation of lime and phosphoric acid, the desirability of determining the effect of higher concentrations of sulfur dioxide was apparent. To this end two procedures appeared possible. To increase the pressure in the vapor phase by increasing the partial pressure of sulfur dioxide, and at the same time have an uniform pressure in a series of bottles involved serious experimental difficulties. The alternative method of determining the possible isotherms at 0°C was adopted. As a matter of fact, the concentrations of sulfur dioxide in the liquid phases were but slightly higher than in the solutions maintained at 25°C. But the relative solubility of lime was much increased, at least in the solutions in contact with calcium sulfite as a solid phase. It appears, therefore, that increasing the partial pressure of sulfur dioxide in the vapor phase will decrease the ratio of phosphoric acid to lime in the liquid phase.

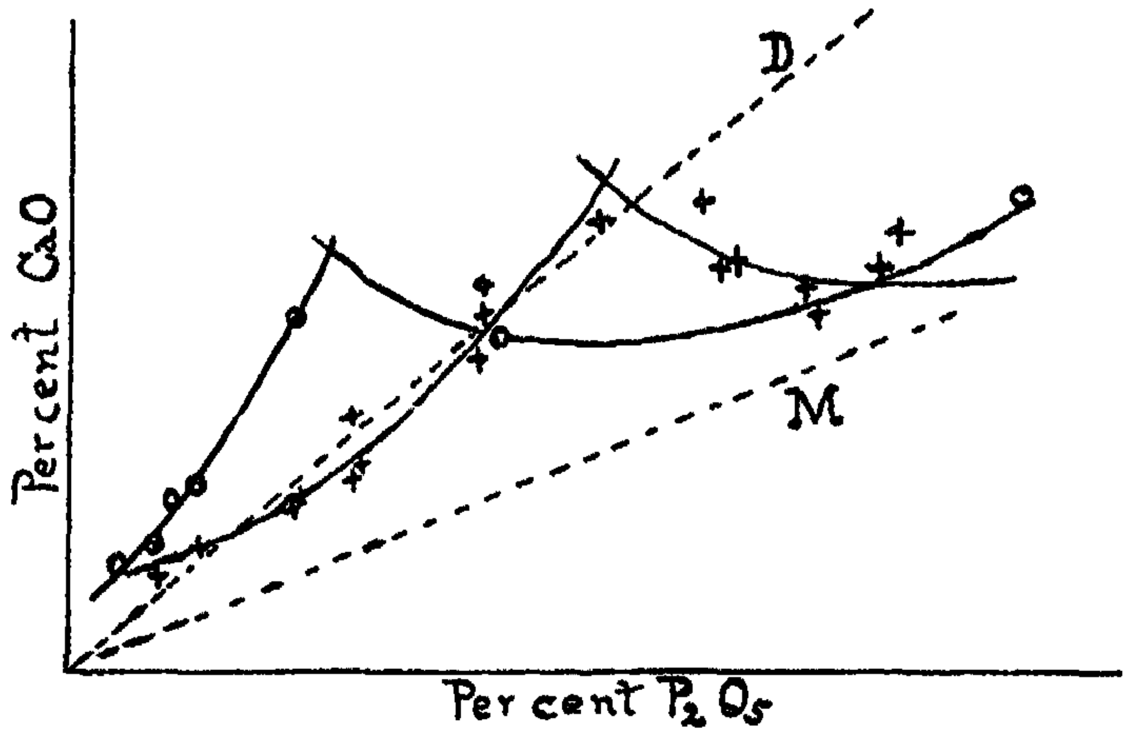

FIG. 2
Solubility isotherms for calcium phosphate in aqueous solutions of sulphur dioxide compared with the loci for hypothetical solutions of dicalcium and monocalcium phosphate, respectively.

For the particular purpose of this investigation it is convenient to plot the results as in Fig. 2. Ordinates represent per cent calcium oxide and abscissae per cent of phosphoric acid. The lines passing through the origin, labelled M and D are the loci of points representing solutions containing phosphoric anhydride and calcium oxide in the ratios of mono- and di-calcium phosphate, respectively. It is apparent that starting with such a product as phosphate rock, contact with saturated aqueous solutions of sulfur dioxide would never produce a solution containing as high a ratio P_2O_5/CaO as corresponds to mono-calcium phosphate. It is feasible, however by successive (or counter current) decantation to obtain a solution with a somewhat higher ratio than corresponds to di-calcium phosphate, the most favorable ratio being with a solution containing about six percent phosphoric anhydride. A roughly approximate but conservative calculation shows that more than 96 percent of the water must be evaporated before the solution would be sufficiently concentrated for mono-calcium phosphate to precipitate. But meanwhile nearly 80 percent of the phosphoric anhydride would have precipitated as the di-calcium salt.

Considering these facts, that a close chemical control would be necessary, that large volumes must be handled and evaporated to produce a moderately priced product, the procedure holds no promise as a practicable plant process. The narrow margins of concentration attainable is a quite sufficient explanation of the failures of previous investigators and inventors.

Summary

1. The addition of sulfur dioxide to aqueous suspensions of the phosphates of calcium increases the solubility of the calcium oxide and of the phosphoric acid.

2. The solubility of the calcium oxide is increased more than the solubility of the phosphoric acid by adding sulfur dioxide.

3. At 0°C or at 25°C there are three solubility curves. On the one corresponding to the lowest concentrations of phosphoric acid, the solubility of sulfur dioxide in the liquid phase, rises to a maximum and then falls again. The solid phases in contact with these solutions are calcium sulfite and a series of solid solutions of calcium oxide and phosphoric acid, a limiting member of the series being di-calcium phosphate. On the second solubility curve, the concentration of sulfur dioxide again passes through a maximum. The solid phases in contact with the solutions represented by this curve are mono- and di-calcium phosphates. A third curve for solutions with relatively high concentrations of phosphoric acid, show negligible and approximately constant content of sulfur dioxide in the liquid phase. Mono-calcium phosphate alone is the solid phase in contact with the solutions represented by this curve.

4. Treatment with sulfur dioxide of an aqueous suspension of a basic phosphate of calcium can yield a solution in which the ratio of phosphoric acid to calcium oxide is somewhat higher than the ratio in di-calcium phosphate. Evaporation of this solution to a concentration at which mono-calcium phosphate would be a stable solid phase involves the loss of 95 percent of the water and the loss of 80 percent of the phosphoric acid as di-calcium phosphate. As a plant method the procedure is impracticable.

5. The facts developed explain the failure of previous investigators and inventors to develop the procedure and obtain mono-calcium phosphate or superphosphates.

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LOW PRESSURE ADSORPTION ON A WASHED GLASS SURFACE*

BY HENRY S. FRANK

The experiments herein described do not constitute as complete an investigation as it was planned to carry out. Although the work had to be discontinued, however, the results obtained are not devoid of interest and bearing upon other current work, and it is considered desirable to report them. The apparatus also presents some interesting features.

The adsorption of water-vapor upon a heavily acid-washed surface of Pyrex was measured at pressures ranging from 5.2×10^{-3} to 8.7×10^{-2} mm. of mercury. The method used was the familiar one of introducing a known amount of water into a space of known volume at a known temperature, and measuring the pressure produced. The amount by which the latter fell short of the value calculated from the gas laws represented the water removed from the gas phase by adsorption on the walls. Since the area of the walls was accurately known, this enabled the amount adsorbed per square centimeter to be calculated for each of a series of equilibrium pressures.

The pressure gauge used was of the membrane, or diaphragm type, but differed from any of the others[1] of which the writer has heard in various respects. It was an all-glass instrument, and utilized a high-frequency "ultramicrometer" method for measuring the movement of the diaphragm.

The Manometer

The instrument is shown in Fig. 1. A is a thin-walled glass bulb, blown on the end of the tube F, and having its end flattened to form a diaphragm. This diaphragm has mounted on it the thin aluminum disc B, which makes no metallic contact with anything except the lead wire 1. A brass collar C, clamped to the tube F, carries three brass rods which support the heavy brass ring R. The circular brass plate P is supported from R by three springs S which are held in tension by screws brazed in P and passing loosely through R. These are held below R by knurled nuts N (only two shown) which thus serve to make the position of P adjustable. A hole in the center of P allows B to hang below it, B and P thus forming a parallel-plate condenser, with adjustable plate-separation. Through N, R and C, P is in metallic connection with the lead 1'. The proportions are about as shown, and the overall diameter of the ring R is just under 5.75 cm. The whole is surrounded by a

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* Contribution from the Chemical Laboratory of the University of California.

[1] Cf. for example Scheel and Heuse: Verh. deutsch physik. Ges., 1909, 1; Fry: Phil. Mag., 25, 494 (1913); Baume and Robert, Compt. rend., 168, 1199 (1919); Daniels and Bright: J. Am. Chem. Soc., 42, 1131 (1920); Karrer, Johnston and Wulf: J. Ind. Eng. Chem., 14, 1105 (1922); Whiddington: Phil. Mag., 46, 607 (1923); Smith and Taylor: J. Am. Chem. Soc., 46, 1393 (1924); Klemenc: 47, 2173 (1925); Allsop: Safety in Mines Research Board, Paper No. 16 (1925).

glass shell of internal diameter 5.75 cm., with a ring seal at D and a side tube T of 2.2 cm. diameter. The latter is so located that before it was sealed off at E the nuts N could be adjusted by means of a stiff wire. The tube F had a bore of 11 mm., and the by-pass G, which carried the stop-cock H was of 5 mm. tubing. The tube communicated with the vacuum line at K. The whole instrument was of Pyrex, and when in operation was immersed to the level of D in a thermostat.

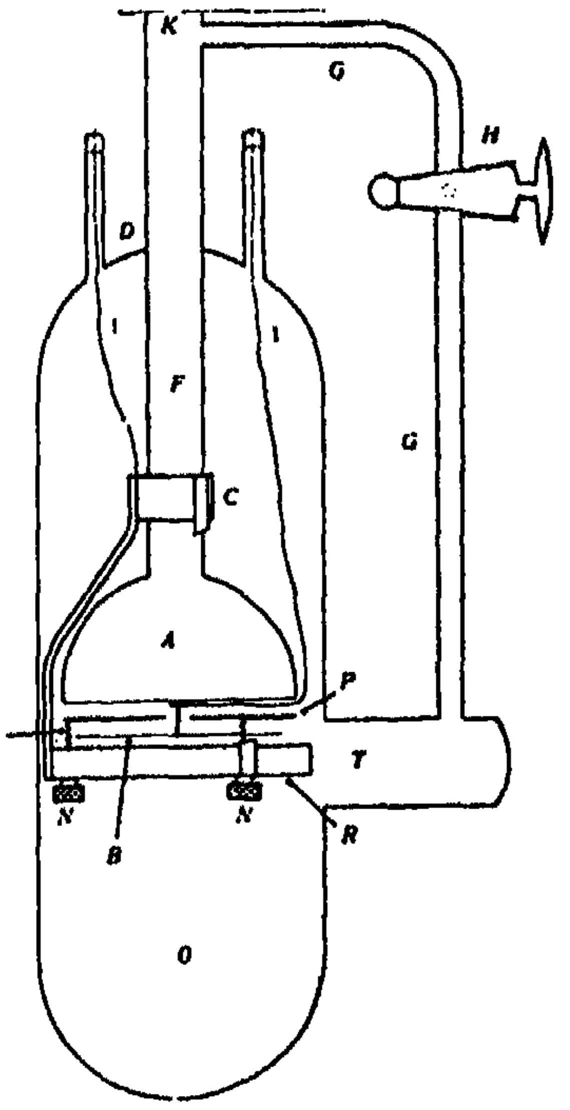

Fig. 1

It is obvious that the greater the area of the plates and the smaller the distance separating them the greater will be the change in capacity for a given small displacement of the diaphragm. In this instrument an upper limit is placed on the area by the exigencies of glass-blowing and a lower limit on the separation by the accuracy to which a thin aluminum plate can be made plane and the steadiness with which it can be supported by the glass diaphragm. The distance which was found practicable for the separation of B and P was of the order of tenths of a millimeter.

The Electrical System

The ultramicrometer circuit used is one given by Gunn.[1] Fig. 2 represents the arrangement used. O is an oscillator operating at about 1,500 kilocycles. R is Gunn's circuit, with X representing the plates of the pressure gauge. The sensitivity claimed by Gunn was not attained; but the sensitivity which was attained was satisfactory for the purpose at hand. Due to fluctuations in the operation of batteries and tubes the following arrangement was also used: A two-way switch was inserted between C_4 and X which made connections alternatively with the manometer or with a fixed air condenser of about the same capacity. During the course of an experiment enough observations were made with this condenser substituted for the manometer to enable a plot to be made of corrections to be applied to the readings made with the manometer. The results obtained were in the main satisfactory.

The manometer was calibrated by comparison with a McLeod gauge, using air dried in a liquid-air trap. The calibration curve was always linear over the range employed, but its slope was found to change somewhat over

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[1] Gunn: Phil. Mag., 48, 224 (1924).

a period of weeks. A few calibrating observations were therefore included in each experiment. There was no hysteresis in the membrane within the limits of accuracy of observation. The probable error in a pressure measurement was about 5×10^{-4} mm.

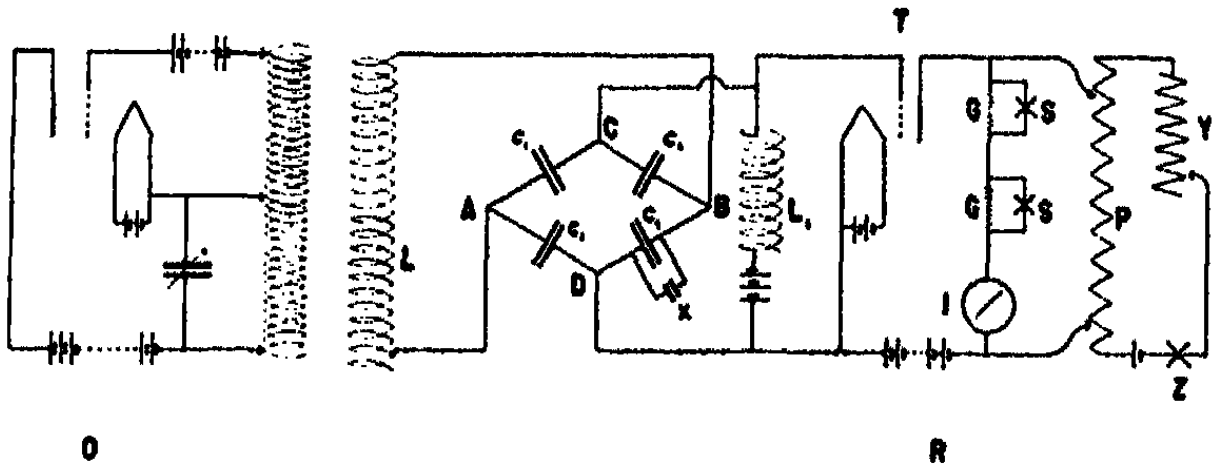

FIG. 2

Measurement of Adsorption

The adsorption apparatus is shown in Fig. 3. G is the manometer, and D is the by-pass (not shown) corresponding to GH of Fig. 1. A is the adsorption chamber, consisting of a number of coaxial Pyrex tubes, bossed to keep their services apart. The innermost tube is sealed shut, enclosing a thermometer. Between marks on the upper and lower tubes A presents an internal area of 8120 sq. cm. and a volume of 2200 cc. The over-all length of A is about 50 cm. and the overall diameter about 8 cm. B is a manifold giving entrance to several capsules E which serve to introduce the water-vapor. The trap K and the stop-cocks F and H are used to admit small charges of dry air for calibration purposes, the reading of the manometer being compared with the pressure shown by the McLeod gauge (not shown).

A detail of the capsule is shown in Fig. 4. It is first weight-calibrated for the volume from the tip of the capillary to the constriction. It is then sealed onto a vacuum line at P, and evacuated for 10 hours or more, during which time it is several times heated just below the softening temperature. (The constriction is actually softened and becomes quite flexible during the heating.) It is then allowed to stand overnight in communication with a cell containing carefully boiled-out water which is maintained at 0°C. Rapid sealing off at the constriction thus gives a bulb of known volume, containing water-vapor at a known pressure. This water is introduced into the adsorption vessel by breaking the capillary tip by means of the slug S.

The adsorption chamber A after leaving the glass-blower was allowed to stand for one week filled with chromic acid cleaning solution, which was several times heated to boiling. The vessel was then rinsed with distilled water, and finally washed seventeen times with conductivity water. It was then sealed onto the apparatus and dried under vacuum.

Fig. 3 does not show a large balloon flask above which communicated with the main vacuum line through a wide-bore stop-cock. It was evacuated before an experiment was begun and the stop-cock then closed. Opening the stop-cock when the system contained water-vapor suddenly lowered the pressure and enabled the adsorption equilibrium to be approached from the high-pressure side.

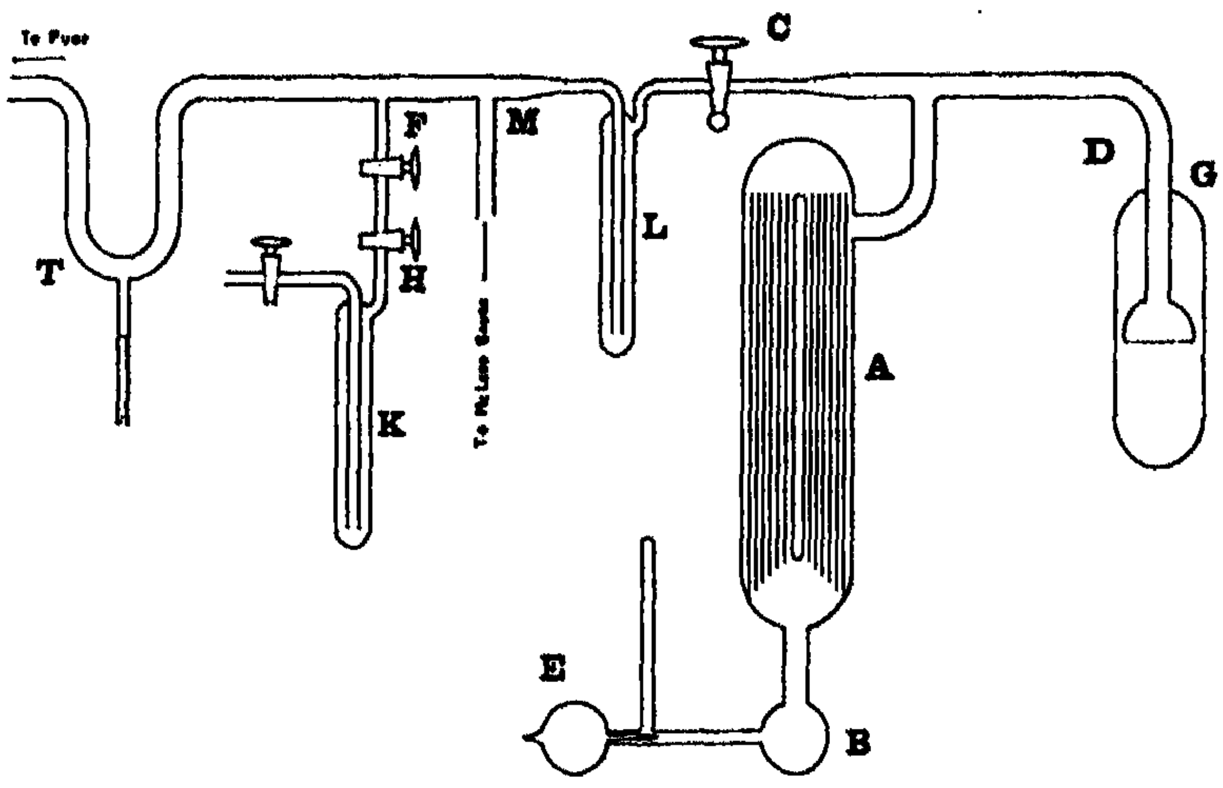

FIG. 3

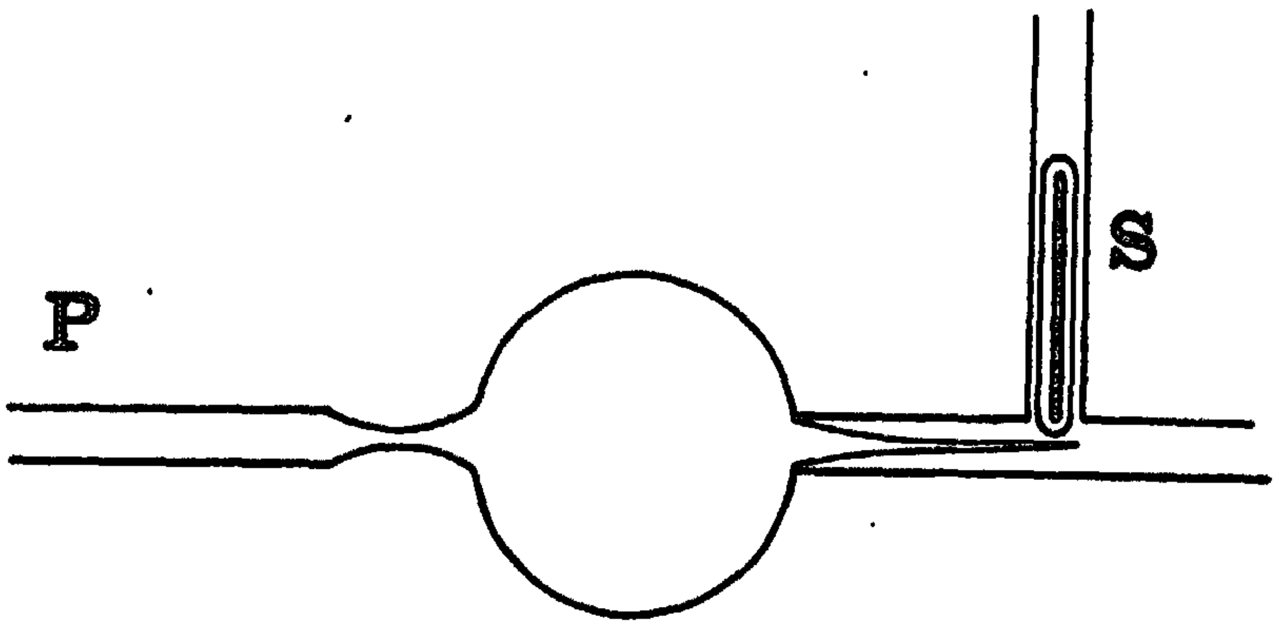

FIG. 4

In carrying out a run, the whole system (Fig. 3) was first evacuated, stop-cocks C and D being open, F and H closed, and liquid air surrounding the traps K and L. Several readings were then taken with the manometer to establish its zero. Stop-cocks C and D were then closed, and the capsules E discharged successively into the system. After each tip was broken sufficient time was allowed to pass for equilibrium to be established. At such time as was desired the large stop-cock was opened to admit vapor into the reserve balloon described above. When as many readings had been taken as were desired, the stop-cock C was opened and the system evacuated. Trap T was then closed, and stop-cocks F and H used to admit successive charges of dry air for calibrating the manometer. T and D were finally opened, terminating the run.

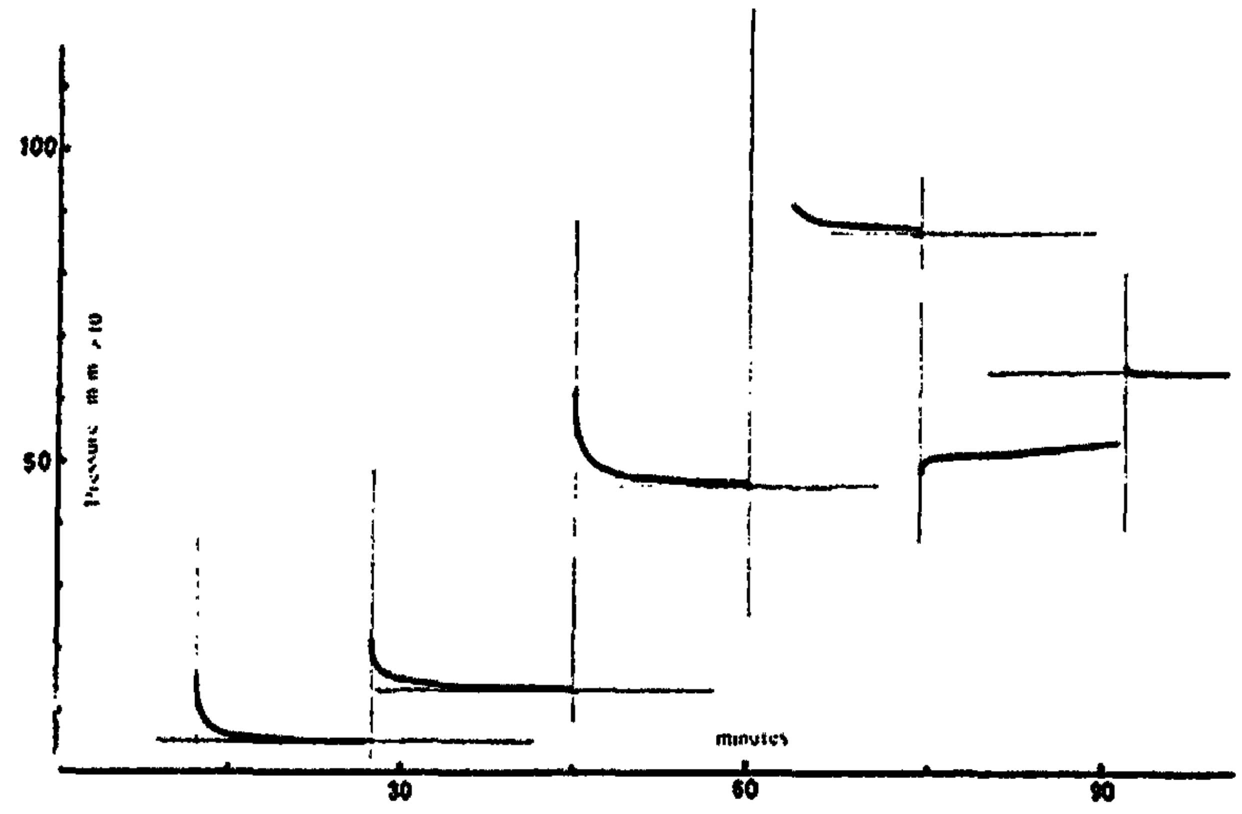

Fig. 5

TABLE I

Point	n′	P	n″	n	A	L
1	0.576	5.2	0.072	0.504	9767	0.50
2	1.15	13.4	0.186	0.964	9817	0.952
3	2.57	46.2	0.656	1.914	9883	1.88
4	3.91	87.0	1.25	2.65	9949	2.58
5	3.28	64.8	0.945	2.33	9984	2.27

These data are represented graphically in Fig. 6.

n′ = Total amount of water in system, in mols × 10^{-5}.
n″ = Amount of water in gas phase, in mols × 10^{-5}.
n = n′ − n″ = Amount of water adsorbed, in mols × 10^{-5}.
L = Thickness of adsorbed layer, in molecules.
P = Observed pressure, in millimeters × 10^{-3}.
A = Area of surface in square centimeters.

Fig. 5 shows graphically the results of such a run, in which the introduction of water vapor was begun within an hour of the time that a good vacuum (less than 1 × 10^{-4} mm.—unreadable on the McLeod gauge) had been established. Here pressures observed are plotted against elapsed time during the experiment. The discontinuities in pressure show when capsules were broken, or in the case of the one at time 84 minutes, when the reserve cock was opened. The capsules were not all of the same size, so that the curve gives no indication on its face of the adsorption isotherm which it represents. It will be noted that the increase in pressure—de-adsorption, that is, following the opening of the reserve cock—was still proceeding at a considerable rate when the last capsule was broken, but that the amount of water-vapor introduced by that capsule was apparently just enough to produce equilibrium. This is confirmed by the fact that on the adsorption isotherm the point corresponding to this equilibrium, reached in so roudabout a way, falls, as nearly as can be ascertained, just in the line of the other equilibria.

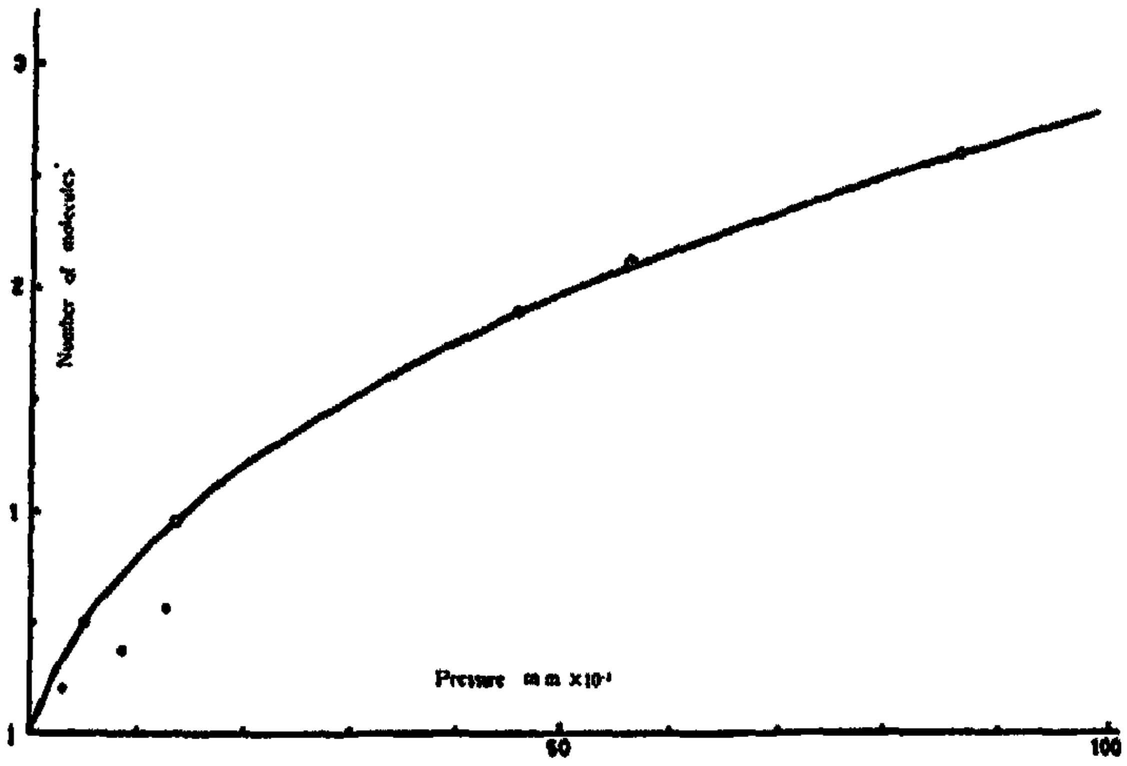

Fig. 6

The isotherm itself is shown in Fig. 6. Here the amount of water adsorbed per square centimeter of glass surface is plotted against the equilibrium pressure. The unit of amount adsorbed per square centimeter is so chosen that unity represents the amount of water which would produce a single layer one molecule deep on the surface, assuming the latter to be plane and the water molecule to occupy it on a square 4 Ångström units on a side. This is the average dimension given by kinetic theory calculations and X-ray measurements on ice crystals. The data from which Fig. 6 is taken are summarized in Table I. The observed pressures were read from a large scale copy of Fig. 5, the asymptotes shown being those chosen as representing the equilibrium pressures.

Since the amount adsorbed is calculated from a difference which is large compared with the subtrahend, i.e. the observed pressure, any error in the latter produces only a much smaller one in L. Trial calculations show that an error of 1×10^{-3} mm. in the assumed asymptotes for the equilibrium pressure—which is much too large to be admissible—would move point 4 by an amount about equal to the thickness of the line representing the curve.

The measurements represented by the square points on Fig. 6 were made in an earlier run before the necessity was apprehended of heating the capsules under vacuum before filling them. The capsules used in this run therefore undoubtedly contain some foreign gas. The effect of this is to make the equilibrium pressure too high, and the apparent adsorption (i.e. difference between computed pressure and observed equilibrium pressure) too low. This would make the points lie below and to the right of the true curve, as in fact they do.

Discussion

Fig. 5 shows that the adsorption process involved here is slow—i.e. a steady state is not, in general, reached in 15 minutes. The good agreement of point 5 with the curve drawn through the other points in Fig. 6, however, indicates that the process is reversible. There is apparently no critical importance attaching to a layer-thickness of one molecule. This, together with the slowness, constitutes evidence against the applicability of the Langmuir theory of adsorption to the process here in question.[1] Indeed this experiment can be regarded as lending strong circumstantial support to the conclusions of Frazer, Patrick, and Smith,[2] and of Latham[3] regarding the nature of acid-washed glass surfaces. That is, these results are entirely compatible with the view that such a surface is covered with a layer of silica gel, and are difficult to reconcile with the contrary view that such a surface is plane. The new experiments of Frazer,[4] giving optical measurements of adsorption of water vapor upon freshly fractured glass surfaces are further evidence that the surface here in question is of a very different nature.

The measurements correspond to a temperature of 20°C. The manometer was thermostated at 25°, but its surface was less than 2% of the total internal area exposed, and it is not felt that this temperature difference played any significant part in the result.

The writer gratefully acknowledges the encouragement and guidance given this work by Professor G. N. Lewis.

Summary

An all-glass membrane manometer has been constructed, suitable for measuring pressure differences up to 0.1 mm. to the thousandth of a millimeter of mercury.

This manometer has been used to measure the adsorption of water vapor on a washed Pyrex surface.

The probable nature of the glass surface is discussed in the light of the results obtained.

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[1] Since the Langmuir theory assumes the existence of a plane surface. Compare, however, Langmuir: J. Am. Chem. Soc., **40**, 1361 (1918); and Carver: **45**, 63 (1923).

[2] Frazer: Patrick and Smith: J. Phys. Chem., **31**, 897 (1927).

[3] Latham: J. Am. Chem. Soc., **50**, 2897 (1928).

[4] Frazer: Phys. Rev., **33**, 97 (1929).

A STUDY OF THE SOLUBLE LAKES OF AURINTRICARBOXYLIC ACID

BY WALTER E. THRUN

Most of the previous work on soluble lakes, such as the alumina lakes of aurintricarboxylic acid and of alizarine monosulfonic acid has been done, with a view to make them useful analytically.[1-8] Atack[1] is of the opinion that the alumina lake formed with sodium alizarine sulfonate is a definite chemical compound. Yoe and Hill[7] present data which support this view, but suggest the likelihood of an equilibrium. This paper attempts to formulate the relations between lake color intensity and the relative amounts of alumina and aurintricarboxylic acid used to prepare the lake solutions. The lakes of other metals with this dye are less intensively studied.

The alumina lake solution of the dye is usually prepared by treating an acid solution of alumina containing ammonium salts, with an aqueous solution of the dye. After allowing a period of time for the lake to form, the color of the excess dye is discharged by making the solution alkaline.

Before presenting the chief data of this paper it may be well to discuss the properties of the alumina-aurine lake. Yoe and Hill[6] found that the lake reached a stable state two hours after making the solution alkaline to a pH probably between 8 and 9. This would indicate that there is an equilibrium between the alumina, which at that pH is somewhat soluble even in the presence of ammonium salts, and the dye, which in presence of ammonium salts exists almost entirely as the non-lake forming anhydride. In the present work it was found that the lake is very stable at a pH of 7.0 ± 0.2. At this pH the color of a "blank" in presence of ammonium salts is completely discharged. The lake color intensity was repeatedly compared with that of an acid solution of thymol blue containing ammonium chloride a few minutes after neutralization and again 24 hours later. No change in relative color intensity as determined with a Dubosque type of colorimeter occurred. When the pH of the lake solution is kept at 7.0 it can be diluted without destruction of the lake.

It was found also that the lake color intensity obtained was the same whether the lake formation occurred at room temperature for 24 hours, or at boiling temperature for one minute followed by rapid cooling, or at 60°

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[1] Atack: J. Soc. Chem. Ind., 34, 936 (1915).

[2] Hammet and Sottery: J. Am. Chem. Soc., 47, 142 (1925).

[3] Lundell and Knowles: Ind. Eng. Chem., 18, 60 (1926).

[4] Middleton: J. Am. Chem. Soc., 48, 2125 (1926).

[5] Corey and Rogers: J. Am. Chem. Soc., 49, 216 (1927).

[6] Yoe and Hill: J. Am. Chem. Soc., 49, 2395 (1927).

[7] Yoe and Hill: J. Am. Chem. Soc., 50, 748 (1928).

[8] Myers, Mull, and Morrison: J. Biol. Chem., 78, 595 (1928).

for ten minutes followed by rapid cooling. Boiling the dye solution before use increases its red color, but no increase in lake color intensity was obtained even when relatively small amounts of dye were used.

A flock is formed when alumina is present in excess. This flocculation can be prevented by the addition of 0.5 ml 1% solution of gum arabic to 50 mls solution. The same color intensity of the lake is obtained in solutions in which no flock forms whether gum arabic is present or not.

The volume of the solution during lake formation was found by Yoe and Hill[6] to affect the color intensity of the lake. This is due to changes in acidity, there being insufficient buffer present to maintain the same pH when the solution is diluted, and to the short time allowed for lake formation. When the solution is acid, the volume and pH have no effect on the final color intensity provided enough time for full development is allowed, or heat is used to accelerate lake formation. Calculations will be discussed later tending to show that the lake formed at room temperature for 24 hours at a pH of 5.1 and kept at that pH has the same color intensity as the lake which has been formed under the same conditions but neutralized to pH 7.0

The color intensity increases with the increase of dye-alumina ratio until a maximum intensity for a given quantity of alumina is reached. The quantities used in this work are of the order of 10^{-6} mole. Therefore the maximum color intensity obtained from 10^{-6} mole $AlCl_3$ with the use of excess dye will hereafter be referred to as the color intensity of one mole lake.

Preparation of Solutions

The aluminium chloride solution was obtained by dissolving the purest metallic aluminium in hydrochloric acid and diluting the resultant solution so that 2.70 c.c. of it contained 10^{-6} mole of aluminium chloride. The ammonium salt of aurintricarboxylic acid known commercially as "aluminon" was dissolved in distilled water to give a 0.001M solution. The chromic chloride solution used was obtained by reducing a known volume of standard potassium dichromate solution by boiling with alcohol and HCl. When the alcohol was boiled off, the solution was diluted to make it 0.001 molar. The 0.001M solution of ferric chloride was made by dissolving a weighed amount of iron wire in HCl, oxidizing the iron with nitric acid, and boiling off the excess acid. This solution was then properly diluted. Ferrous chloride solution was obtained by dissolving a known weight of standard iron wire in HCl. This solution was then diluted with recently distilled water to make it 0.001 molar. It gave an exceedingly small positive test for ferric iron with KCNS. A small amount of N/10 sodium thiosulfate was always added to the reaction mixture in order to insure reduction of any ferric iron and to prevent oxidation during the experiments. The dihydrate of berylium chloride, a c.p. commercial preparation, was dissolved to give a 0.001 molar solution. The concentration of this was checked by titrating the chlorine with a standard silver sulfate solution.

Experimental Procedure

The lake was developed in 50 c.c. flasks at a volume of 25 c.c. The solution was 0.3 molar with HCl and molar with ammonium acetate, and contained 0.5 c.c. 1% gum arabic solution. In some of the experiments lake formation was allowed to go for 24 hours at room temperature. In others the lake formation was speeded up by heating to 60° for ten minutes, or by boiling the solution for one minute. Longer boiling has the disadvantage that the color of the excess dye is discharged more slowly after neutralization. The warm solutions were then cooled to 25°, and 5 c.c. of 5M ammonium chloride were added. Then 5 c.c. of ammonium carbonate were added with shaking,

TABLE I

10^{-6} mole $AlCl_3$	10^{-6} mole ammonium aurin tricarboxylate	10^{-6} mole lake	K
3.00	3.00	1.08	1.25
2.50	1.41	0.48	1.56
2.00	0.86	0.26*	2.00*
2.00	0.94	0.32	1.63
2.00	1.00	0.34	1.60
2.00	1.00	0.33	1.69
2.00	1.30	0.41	1.72
2.00	1.60	0.50	1.65
2.00	2.26	0.74	1.30
2.00	2.48	0.78	1.33
2.00	4.00	1.08	1.25
2.00	6.00	1.32	1.42
1.48	2.00	0.61	1.33
1.00	1.50	0.41	1.56
1.00	1.80	0.48	1.43
1.00	2.00	0.51	1.43
1.00	2.00	0.53	1.30
1.00	2.01	0.48	1.64
1.00	2.55	0.59	1.36
1.00	3.00	0.64	1.33
1.00	3.00	0.63	1.39
1.00	3.60	0.67	1.44
1.00	4.00	0.705	1.37
1.00	4.00	0.68	1.56
1.00	4.10	0.74	1.17
1.00	4.55	0.78	1.07
1.00	6.00	0.81	1.21
1.00	6.00	0.80	1.30
1.00	8.00	0.86	1.17
		Ave.	1.41

* Not used in average.

whereupon the solution was immediately diluted up to the 50 c.c. mark and again shaken. The ammonium carbonate was of such concentration (about 2.4M) that a blank run without dye in the same way had a final pH of 7.0 (determined colorimetrically). It was found that shaking the solution with a drop of octyl alcohol would prevent the escaping carbon dioxide bubbles from collecting on the colorimeter prisms.

Quantities were measured out in pipettes. The same volumes for all comparative data were insured by the use of the same pipettes always for the same reagent.

Ammonium carbonate, rather than ammonia, was used to neutralize the solution because thereby local areas of high pH are avoided. The ammonium chloride was added because the red color of the unadsorbed dye is more quickly destroyed in presence of large quantities of ammonium salts.

The "blank" (without alumina) will become colorless (or take on a straw yellow color when much dye is present) if the above procedure is followed.

For a part of the work a permanent standard color solution of thymol blue was used. Later all comparisons of color intensities were made against a solution containing one "mole of lake." The comparison of a deeply colored with a much less colored solution was often accomplished by comparing both solutions with a solution of intermediate color. Comparisons of color intensity were made with a Dubosque type of colorimeter.

The data presented in the tables were obtained by the above procedure. For the work presented in the first part of this paper the changes in the above procedure are obvious.

Discussion of Results

The results for alumina are given in Table I. The values for K are calculated on the following assumptions. Two molecules of aurintricarboxylic acid are adsorbed by or combine with one molecule of the hydrous oxide of aluminium. "Free" aurine is that part of the dye which has not been adsorbed by the alumina. "Free" alumina is that part of the alumina which has not adsorbed any dye. The relations are shown by the following equations:

$$\frac{(\text{free } Al_2O_3)\ (\text{free aurine})}{(\text{total } Al_2O_3)\ (\text{lake})} = K$$

or

$$\text{lake} = \frac{1}{K}\ \frac{(\text{free } Al_2O_3)\ (\text{free aurine})}{\text{total } Al_2O_3}$$

When the solution for the volume used (50 c.c. here) contains one-half mole alumina the equation is simplified to:

$$\text{Lake} = 1/K\ (2 \text{ free } Al_2O_3)\ (\text{free aurine})$$

If the data are accepted we have a constant similar to the ionic dissociation constant except that dilution does not enter as a factor.

Before discussing the accuracy of the value obtained for K, it is well to mention the fact that the value 1.41 for K was checked repeatedly by using it to calculate the concentrations necessary for two solutions to give the same color intensity, one of them containing a relatively small amount of alumina and a large amount of dye, the other containing a large amount of alumina and a small amount of the dye. In every experiment no difference in color intensity was observed.

The variations in the values for K given in Table I may be explained as due to several factors. The errors of the colorimeter readings were in the neighborhood of 5%. These would then account for variations of 0.07 from the true value. In general, the values obtained when relatively small amounts of alumina were present are higher than the average, and those obtained when the amount of dye used was relatively large are lower than the average. One reason for this lies in the fact that a large excess of dye is not decolorized upon neutralization, but gives a straw yellow color. This tends to give a total color intensity of the standard solution (containing one mole lake prepared by use of large excess of dye) which is too high, and the results with small quantities of dye will be too low. It is also possible that the lake is not quite so stable when small quantities of dye are used. It is the red acid-stable form of the dye which forms lakes, and this does not exist to any extent in neutral solutions containing ammonium salts. The possible existence of a trend in the values for K may be due to differences in stability of the lakes.

A series of lake solutions made up to volume at pH 5.1 was compared with a series which had been neutralized to pH 7.0. Using the value 1.41 for K the color intensity of the lake was calculated. The difference in color intensity of the acid solution over the neutralized solution was assumed to be due to the excess dye. The values obtained experimentally checked reasonably well with those calculated, thus indicating that the lake color at pH 5.1 is of the same intensity as when neutralized to pH 7.0.

Table II shows the results obtained with the salts of other metals. The values for K were obtained by first running several series of different metal aurine ratios and using the maximum color intensity obtainable from one mole metal as the basis of comparison. The approximate value for K was then calculated and checked, as was the constant for alumina, by comparing the colors of two solutions which, though having different metal aurine ratios, should have the same color intensity.

When the ferric oxide lake is formed at room temperature it has a violet purple color with no, or very little red. When it is formed at higher temperatures, it takes on more of a red color. This ability of ferric oxide to form two differently colored lakes may be due to different states of hydration of the hydrous oxide. In the absence of ammonium salts ferric oxide can form a straw colored lake. This lake is usually formed in neutral or alkaline solutions when the blank shows some pink color. The orange color was deeper than the blank pink and the yellowish iron oxide color (obtained under the same conditions without the dye) superimposed upon each other.

TABLE II

Metallic salt used	Color of Lake	Stability at pH 7.0	K
$FeCl_3$	violet purple	xxxx	0.15
$AlCl_3$	red	xxx	1.41
$CrCl_3$	red	xxx	1.41
$FeCl_2$	red	xxx	1.61
$BeCl_2$	red	x unstable in absence of excess dye	2.22
$MgSO_4$	pink	stable in alkaline in absence of ammonium salts	very large
$Ti_2(SO_4)_3$	Increases yellow color of "blank."		

The chromium oxide lake is about as stable as the alumina lake. Its color is, however, not quite so deep as that of the alumina lake.

The ferrous oxide lake, unlike that of magnesium oxide, is quite stable in the presence of ammonium salts. The solubility of magnesium hydroxide in ammonium salts is responsible for the instability of the magnesium oxide lake.

The berylium oxide lake is only stable in presence of a large excess of the dye. Berylium oxide is probably too soluble at the neutral point.

Kolthoff[1] gives directions for preparing the curcurmin lake of beryllium oxide in a more alkaline solution. Titanic sulfate under conditions obtaining in this work increased the straw yellow color of the blank. It may be possible that it forms a straw colored lake with the anhydride of the dye.

This suggests that aurintricarboxylic acid can form two different kinds of lakes. The first is formed when the acid (red) form is adsorbed by a hydrous oxide which is insoluble in slightly acid solution. The other kind is formed when the anhydride is adsorbed by an insoluble base like ferric hydroxide in absence of ammonium salts, or by a negative hydrous oxide like the titanic in presence of ammonium salts.

The values for K given in Table II multiplied by 10 will give approximately the number of moles of the dye required to give maximum lake color intensity with one mole of metal salt under the conditions given here. Since a curve plotted showing color intensity against dye concentration has only a very slight trend when the color intensity is near the maximum, these figures cannot be checked accurately.

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[1] Kolthoff: J. Am. Chem. Soc., 50, 393 (1928).

These figures show that the lake formation is dependent upon the insolubility of the hydrous oxides of the metals. However, the presence of a large excess of dye counteracts the solution of the hydrous oxides, and, if given enough time, causes the formation of as much lake as if the hydrous oxide were almost completely insoluble.

Summary

1. The equilibrium relations existing between alumina and aurintricarboxylic acid and the resulting lake formed have been formulated.
2. The equilibrium relations of the aurintricarboxylic acid lakes of a number of other metals are given for the same conditions as were found best for alumina.
3. The work suggests the existence of two different kinds of lakes of the dye.
4. The solubility of hydrous oxides of metals is counteracted by the presence of a large excess of the dye to form almost as much lake as if the hydrous oxide were almost insoluble.

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LIQUID MIXTURES OF TELLURIUM AND SODIUM TELLURIDE

I. SPECIFIC RESISTANCE AS A FUNCTION OF COMPOSITION AND TEMPERATURE

BY CHARLES A. KRAUS AND STANLEY W. GLASS

The present investigation was originally undertaken for the purpose of studying the conductance of liquid mixtures of tellurium and sodium telluride. According to Pellini and Quercigh[1] sodium and tellurium are completely miscible in the liquid state with the exception of an interval lying between 25 and 37 atom per cent. of sodium. Their diagram indicates the existence of a normal telluride, Na_2Te, which is quite stable, melting at approximately 1000°, as well as two higher tellurides, to which they assign the formulae Na_3Te_2 and Na_2Te_7. The gap in the solubility diagram occurs in the region corresponding to the composition Na_2Te_7. In carrying out conductivity measurements on various liquid mixtures, the appearance of new phases was indicated by inflection points in the resistance temperature curves. These points did not agree with the earlier data of Pellini and Quercigh and, accordingly, the phase diagram of mixtures of tellurium and sodium telluride was redetermined by the method of thermal analysis. The results of conductance measurements will be presented first since they will later be of assistance in interpreting the phase diagram.

Materials

Tellurium was purified according to the following procedure. The commercial metal was dissolved in dilute nitric acid and the basic nitrate formed was allowed to settle. The supernatant liquid was decanted and evaporated to dryness. The residue so obtained, together with the basic nitrate originally precipitated, was decomposed by heat. This impure oxide was dissolved in hydrochloric acid, and the resulting solution was evaporated to dryness in order to expel traces of nitric acid. The residue was now dissolved in concentrated hydrochloric acid, diluted with an equal volume of water, made slightly alkaline with ammonium hydroxide, and then acidified with dilute acetic acid. The tellurium dioxide precipitated in this process was thrown on a filter, washed and dried. It was then heated to about 600° in a Pyrex tube through which a slow stream of oxygen was passed. This served to remove most of the volatile impurities consisting chiefly of selenium dioxide. The residue was again dissolved in concentrated hydrochloric acid and the solution was saturated in the cold with sulphur dioxide.[2] Selenium was precipitated[3] and separated by filtration through asbestos. The filtrate was

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[1] Atti Acad. Lincei, (5), 19 II, 350 (1910).

[2] Lenher and Kao: J. Am. Chem. Soc., 47, 769 (1925).

[3] Keller: J. Am. Chem. Soc., 19, 773 (1897).

diluted to about 6N and again saturated in the cold with sulphur dioxide in order to precipitate the tellurium. The precipitated metal was filtered and thoroughly washed with water and, finally, with alcohol and dried quickly at 110°C. The metal was then distilled in vacuo in an electric furnace. The purified product gave no evidence of impurities when subjected to a spectroscopic test.[1]

Sodium telluride was prepared by treating a weighed quantity of freshly-cut sodium in liquid ammonia with finely divided metallic tellurium. The metal was added slowly until the blue color, due to free sodium, just disappeared. Sodium telluride Na_2Te is only slightly soluble in liquid ammonia, the saturated solution being colored light yellow. The ditelluride, Na_2Te_2, is readily soluble and yields a highly colored violet-blue solution. The characteristic color effects make it possible to adjust the composition of the product accurately to the formula Na_2Te and the total weight of material is determined from the amount of tellurium added, thus making it unnecessary to weigh the sodium.

The reaction between sodium and tellurium is carried out in a closed tube cooled to liquid ammonia temperatures by means of a bath of boiling ammonia. When the reaction is completed, the ammonia is allowed to evaporate and the necessary quantity of tellurium is added in order to produce an alloy of any desired composition. The tube containing the sodium telluride and tellurium is then heated in an atmosphere of ammonia or nitrogen to a temperature of about 600° and the contents are thoroughly stirred. After allowing the tube to cool, it may be broken and the contents transferred to the measuring apparatus in an atmosphere of nitrogen.

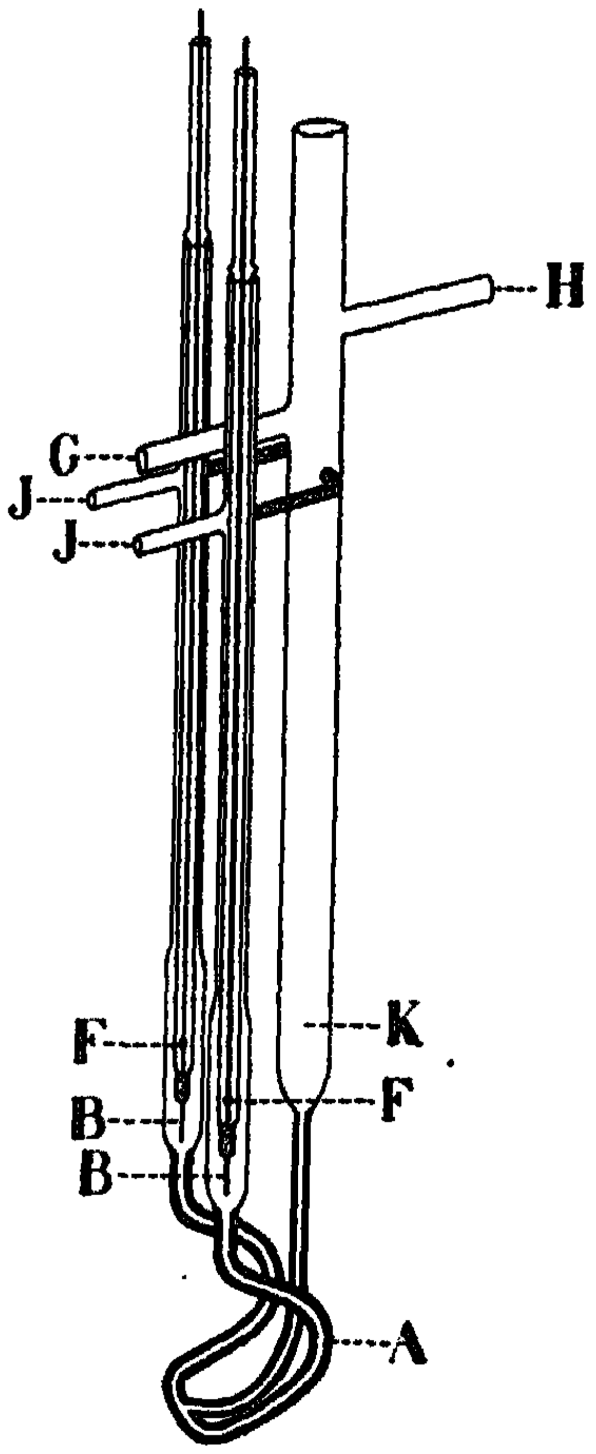

Fig. 1
Cell used in measuring Resistance of Mixtures of Te and Na_2Te

Apparatus and Procedure

Thermostat. The thermostat employed in this investigation was similar to that previously described by Kraus and Johnson,[2] and further description may, therefore, be omitted.

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[1] Dudley and Jones: J. Am. Chem. Soc., 34, 1004 (1912).

[2] Kraus and Johnson: J. Phys. Chem., 32, 1281 (1928).

The Conductivity Cell. In the preliminary measurements, a Pyrex glass cell was employed, similar in construction to the high-resistance cells used by Kraus and Johnson in measuring the resistance of metallic tellurium. It was found, however, that mixtures of sodium telluride and tellurium slowly react with glass so that reproducible results cannot be obtained. Accordingly, a similar cell was constructed of clear fused quartz. The general arrangement of the cell is shown in Fig. 1. The capillary A of this cell had a length of approximately 30 cm. and an internal diameter of 1.5 mm. The electrodes BB, making contact with the melt, were platinized. The process of platinization had to be repeated after each series of measurements, as otherwise, satisfactory results could not be obtained. Copper leads were hard soldered to the platinum electrodes at FF, the junctions being located below the level of the thermostatic liquid in order to avoid thermoelectric effects.

In all, five cells of the type described were employed. Their resistance constants were determined at 25°C by means of a normal solution of potassium chloride made up by weight according to directions of Kraus and Parker.[1] The specific conductance of 1.0 N potassium chloride solution was assumed to be 0.11180. The data relating to the calibrations are summarized in Table I.

TABLE I

Constants of Conductivity Cells

Cell	1	2	3	4	5
Resistance	7248.4	7179.0	7171.0	7161.4	7106.5
Constant	810.4	802.6	801.7	800.6	794.5

Measuring Apparatus. The electrical resistance of alloys of higher specific resistance was measured by means of a drum-wound bridge and telephone. A Vreeland oscillator served as source of alternating current and the usual precautions were taken as to screening, grounding, etc. In the case of alloys, of lower resistance, a direct current with a precision Wheatstone bridge was employed. Polarization was marked in alloys of higher resistance.

The temperature was measured by means of a platinum platinum-rhodium thermocouple, which was calibrated against the boiling point of water and the melting points of standard samples of tin, lead, zinc and aluminum.

Procedure. The alloy, prepared as already described, was quickly transferred into tube K of the conductivity cell under an atmosphere of nitrogen. The cell was then exhausted and repeatedly washed with fresh nitrogen to remove traces of air. Finally, the cell was filled with nitrogen to a pressure approximately 1 cm. above that of the surrounding atmosphere, and this pressure difference was maintained throughout all subsequent operations. Tubes G, J J and H served to make connection to the auxiliary apparatus as described by Kraus and Johnson.

The cell containing the alloy was introduced into the thermostat and heated to a temperature above 500°, or sufficiently high to completely melt

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[1] Kraus and Parker: J. Am. Chem. Soc., **44**, 2426 (1922).

the alloy. By introducing nitrogen through the tubes JJ and the capillary A, the liquid in tube K was stirred. It was then allowed to flow into the capillary making contact with the electrodes BB. The resistance was measured and the process of stirring repeated until constant values were obtained. The resistance was then measured at successively lower temperatures at intervals of from 10° to 25°. When the measurements were completed, the alloy was melted and blown out of the capillary into the tube K by means of nitrogen, after which the cell was removed from the thermostat and the alloy allowed to solidify.

Experimental Data

Composition of Alloys. In Table II are given the data relating to the composition of the various alloys used. Column 2 indicates where the resistance measurements are tabulated. Otherwise the table is self-explanatory. As explained above, the weight of sodium given in column 4 has been calculated from the equivalent weight of tellurium used in the neutralization of sodium, the weight of which is given in column 3. Analytical checks indicated that the composition of the alloys as calculated corresponded closely to the true values.

TABLE II

Data on Preparation of Alloys used in Conductance Measurements

Composition Atom % Na	Table No.	Wt. Te for Na_2Te in g.	Calc. wt. Na in g.	Total wt. Te in g.
54	III	12.042	4.3447	20.517
50	IV	11.179	4.0331	22.357
48	V	9.927	3.5816	21.509
46	VI	9.416	3.3971	22.107
44	VII	8.701	3.1392	22.156
40	VIII	9.293	3.3530	27.880
35	IX	6.403	2.3103	23.784
30	X	5.393	1.9459	25.171
25	XI	4.298	1.5507	25.778
20	XII	3.028	1.0924	24.223

TABLE III

Resistance of Alloy, $Na_{54}Te_{46}$, Cell No. 5

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
503.1	1.732	0.5774	456.0	0.4593	2.177
480.6	1.503	0.6654	436.2	0.2900	3.448
461.9	1.319	0.7580			

Results. The specific resistance of the various alloys at different temperatures are given in Tables III-XII. The composition of each alloy and the cell used are indicated at the head of the several tables. In Figs. 2, 3 and 4, the specific resistance is plotted as a function of the temperature for alloys corresponding to the compositions $Na_{50}Te_{50}$, $Na_{40}Te_{60}$ and $Na_{25}Te_{75}$ respectively. The curves for other compositions are similar to one or another of the three reproduced in the figures. In Fig. 5 values of the specific resistance are plotted as a function of the composition at different temperatures.

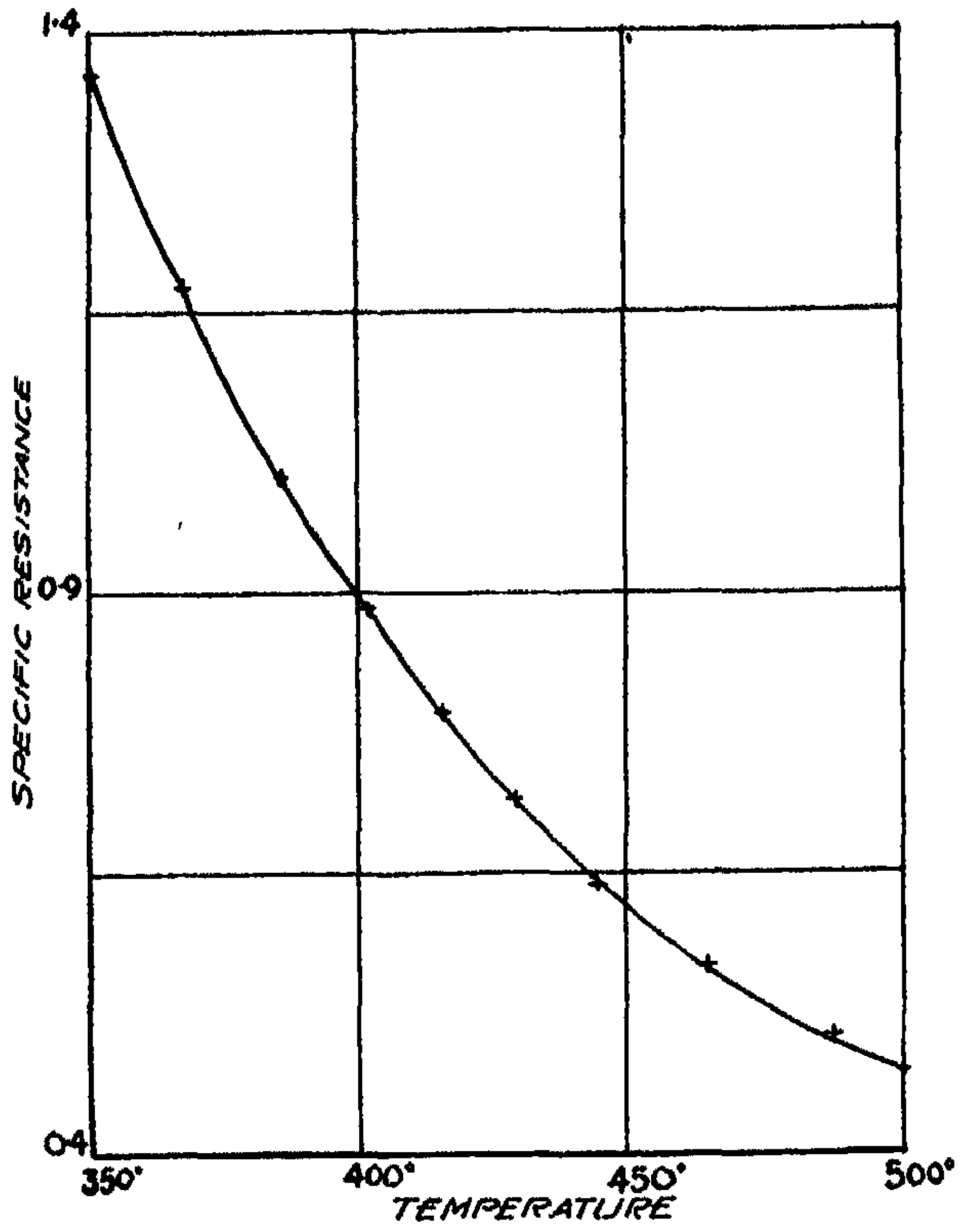

FIG. 2
Resistance Temperature Curve of Alloy $Na_{50}Te_{50}$.

TABLE IV

Resistance of Alloy, $Na_{50}Te_{50}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
500.4	2.106	0.4749	402.2	1.129	0.8858
487.6	1.977	0.5057	386.4	0.9966	1.0034
464.5	1.754	0.5701	367.4	0.8526	1.173
446.3	1.562	0.6402	350.2	0.7338	1.363
430.1	1.394	0.7173	328.6	0.1902	5.258
416.0	1.257	0.7957			

TABLE V

Resistance of Alloy, $Na_{48}Te_{52}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis	Temp.	Sp. Cond.	Sp. Resis
497.2	2.357	0.4243	399.4	1.312	0.7624
480.0	2.134	0.4690	381.1	1.159	0.8629
458.1	1.893	0.5282	358.6	0.9766	1.024
438.0	1.674	0.5975	324.8	0.4062	2.462
410.0	1.408	0.7100			

TABLE VI

Resistance of Alloy, $Na_{46}Te_{54}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
499.6	2.835	0.3527	382.5	1.318	0.7587
483.0	2.555	0.3914	363.2	1.143	0.8745
465.0	2.277	0.4391	349.0	1.011	0.9886
449.9	2.075	0.4819	335.5	0.9016	1.109
431.8	1.851	0.5403	323.9	0.8169	1.224
414.2	1.645	0.6079	Rose suddenly to	0.4404	2.271
396.9	1.457	0.6862			

TABLE VII

Resistance of Alloy, $Na_{44}Te_{56}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
499.3	3.501	0.2856	381.3	1.483	0.6745
475.3	2.930	0.3413	363.2	1.287	0.7772
456.1	2.584	0.3870	347.2	1.128	0.8863
440.7	2.330	0.4292	332.0	0.9841	1.016
419.9	1.992	0.5020	320.4	0.8801	1.136
402.0	1.737	0.5756			

TABLE VIII

Resistance of Alloy, $Na_{40}Te_{60}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
497.3	6.051	0.1653	350.8	1.586	0.6306
467.6	4.648	0.2151	340.9	1.676	0.5968
444.1	3.780	0.2646	334.2	1.626	0.6148
420.0	3.032	0.3298	320.2	1.515	0.6600
394.4	2.402	0.4164	311.3	1.434	0.6975
372.5	1.951	0.5125	297.9	1.000	0.9995
			Reheated and stirred		
354.0	1.630	0.6133	435.0	3.512	0.2847
333.1	1.614	0.6195	409.6	2.769	0.3612
325.2	1.557	0.6422	364.0	1.800	0.5556
319.0	1.500	0.6667	348.0	1.736	0.5761
Reheated and stirred					
426.1	3.253	0.3074	351.0	1.741	0.5743
392.8	2.378	0.4206	358.3	1.735	0.5764
365.3	1.826	0.5477	359.3	1.735	0.5763

TABLE IX

Resistance of Alloy, $Na_{35}Te_{65}$, Cell No. 4

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
511.3	16.08	0.06217	385.1	4.640	0.2155
487.2	12.55	0.07970	368.1	4.101	0.2438
468.0	10.23	0.09772	353.9	3.743	0.2672
452.6	8.658	0.1155	339.1	3.321	0.3011
436.0	7.197	0.1389	328.5	3.029	0.3302
428.5	6.613	0.1512	315.5	2.697	0.3707
414.2	5.618	0.1780	305.2	1.520	0.6580
400.0	4.969	0.2012			

TABLE X

Resistance of Alloy, $Na_{30}Te_{70}$, Cell No. 2

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
506.5	42.92	0.02330	371.4	9.226	0.1084
491.8	35.83	0.02891	356.6	7.848	0.1274
476.3	30.08	0.03324	348.0	7.178	0.1393
451.8	22.55	0.04434	336.9	6.316	0.1583
431.1	17.71	0.05645	323.6	5.419	0.1845
405.1	13.54	0.07385	313.7	4.788	0.2088
387.9	11.02	0.09077	302.9	2.831	0.3532

TABLE XI

Resistance of Alloy, $Na_{25}Te_{75}$, Cell No. 4

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
501.1	102.08	0.00980	364.8	14.76	0.06773
467.7	65.43	0.01528	354.6	12.90	0.07752
443.2	48.31	0.02070	339.5	10.66	0.09383
422.0	30.30	0.03300	324.1	8.710	0.1148
401.7	23.60	0.04236	310.8	7.286	0.1372
389.8	20.33	0.04918	304.9	6.701	0.1492
377.0	17.33	0.05772			

TABLE XII

Resistance of Alloy Na_{20} Te_{80}, Cell No. 3.

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
527.0	250.8	0.003986	374.9	27.59	0.03625
495.4	191.4	0.005225	356.7	22.87	0.04373
471.8	151.7	0.006592	332.0	17.76	0.05631
448.9	117.8	0.008487	315.9	15.04	0.06651
425.0	88.16	0.01134	301.0	12.88	0.07765
404.8	77.72	0.01287			

Discussion

In all cases, the specific resistance of the alloys diminishes markedly with increasing temperature, approximately, according to an exponential function. At higher concentrations of sodium, the resistance increases regularly with decreasing temperature without singularities until a large discontinuous increase of the resistance occurs. This latter change is doubtless due to the appearance of a solid phase. In general, at these higher concentrations of sodium, there was no indication of the initial appearance of a solid phase at temperatures corresponding to the melting point diagram. Transformation was apparently suspended until, when crystalization set in, substantially complete solidification occurred. It may be noted that on investigating the melting point diagram in the same region by the method of thermal analysis consistent results could be obtained only under conditions of vigorous stirring and seeding of the melt. In the case of alloys richer in tellurium, the initial appearance of the solid phase in the neighborhood of the expected temperatures was readily determinable. Under these conditions, the resistance increased continuously with falling temperature until a solid phase began to appear, when the direction of the curve underwent a discontinuous change although the resistance itself varied continuously. This is well illustrated

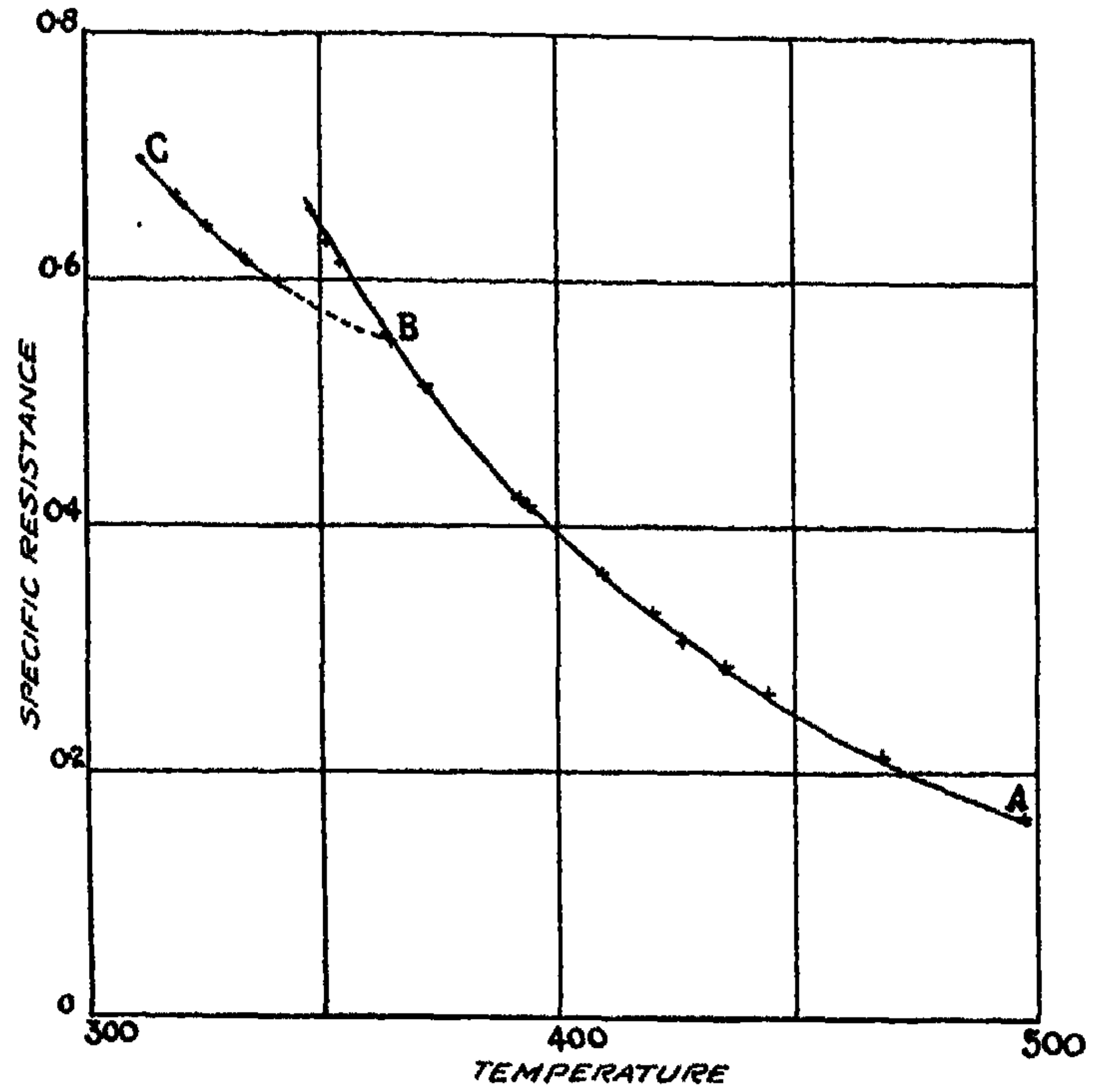

Fig. 3

Resistance Temperature Curve of Alloy $Na_{40}Te_{60}$.

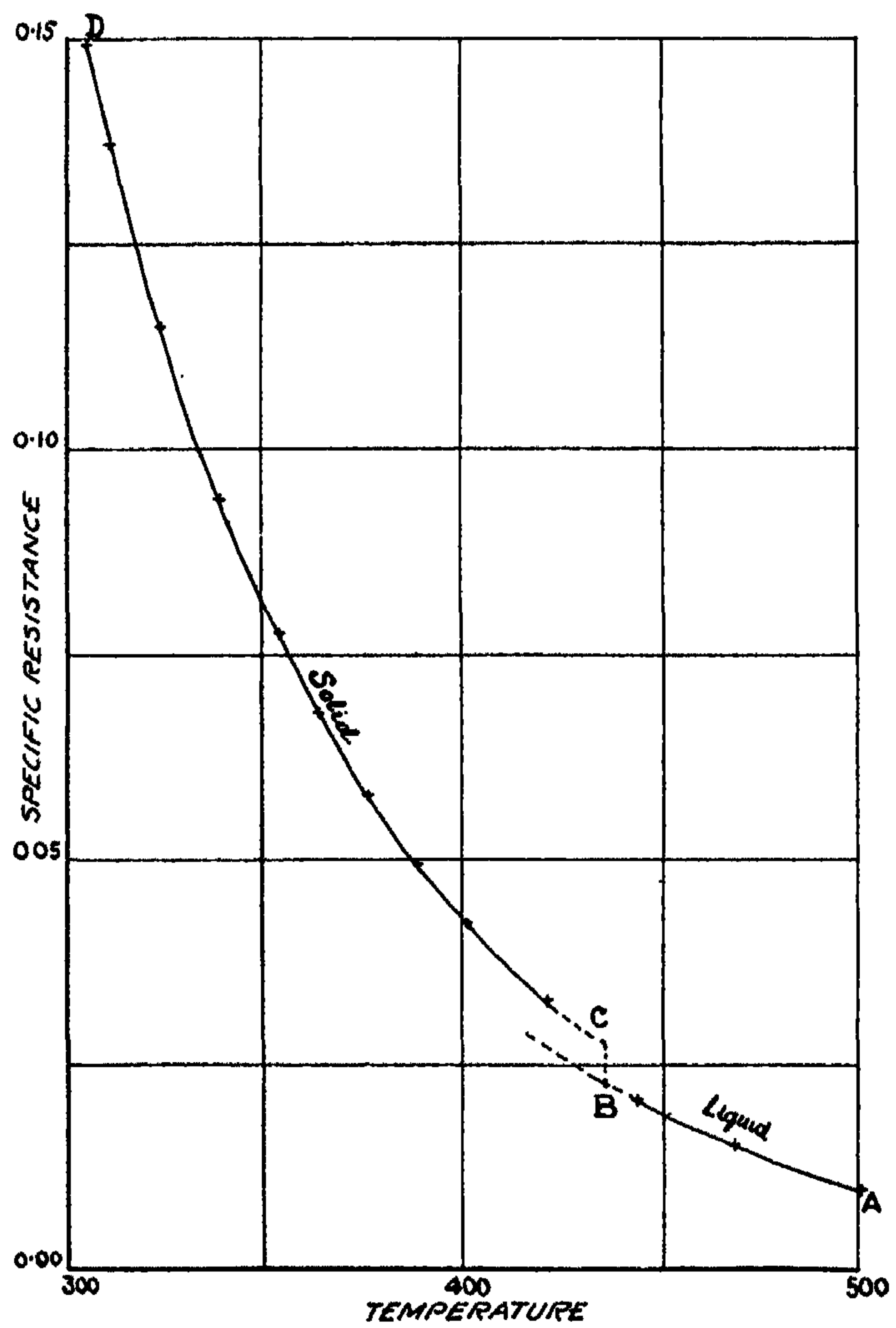

Fig. 4
Resistance Temperature Curve of Alloy $Na_{25}Te_{75}$.

in Fig. 3 with an alloy containing 40 atom per cent. of sodium. Three series of measurements were carried out which showed that the initial point of crystalization lies at approximately 365°. In this case, the liquid phase persisted some degrees into the metastable region, when a discontinuous change of resistance occurred. The temperature at which a solid phase should initially appear can be approximated by extrapolation of the curves to their point of intersection. The resistance of the mixture of liquid and solid is slightly lower than that of the homogeneous liquid at the same temperature. The curve *BC* relating to mixtures of liquid and solid lies below *AB* for the homogeneous liquid. Finally, at still lower temperatures, the eutectic between Na_2Te_6 and Na_2Te_2 is reached and complete solidification occurs with a discontinuous change in the resistance. It was not possible to obtain the exact temperature of the eutectic point by means of the resistance effect owing to suspended transformation. An alloy containing 35 atom % of sodium gave an inflection point at 405° and one containing 20 atom % at 430°.

The alloy containing 25 atom % of sodium showed a small discontinuous change of resistance at 436°. This corresponds to the congruent melting point of the compound Na_2Te_6. The curve *AB* of Fig. 4 relates to the homogeneous liquid alloy of the above composition, while the curve *CD* relates to the homogeneous solid alloy. It will be observed that the solid alloy is a fairly good electrical conductor. Both curves follow an exponential relation quite closely.

By means of the conductivity method, the following points were established on the melting point curve.

Table XIII

Initial Crystalization Temperature by Conductance Method

Atom % Sodium	20	25	35	40
Temp. of initial Cryst.	430	436	405	365

The resistance method is often advantageous in determining the temperature at which a solid phase begins to appear. The two branches of the resistance-temperature curve, relating respectively to the homogeneous liquid and to the mixture of liquid and solid, intersect and the point of intersection may be approximated fairly closely. Suspended transformation merely increases the extrapolation and thus increases the error but the result is definite. In regions where the method of thermal analysis breaks down because of suspended transformation, the conductivity method serves as a valuable supplement to the former. In a succeeding paper, the results, just presented, will be used in interpreting the phase diagram of the system Te-Na_2Te.

In Fig. 5, values of the resistance are plotted as a function of the composition at a series of temperatures.

As may be seen from this figure, the alloys containing higher percentages of tellurium are extremely good conductors. Without doubt, these alloys are true metals: that is, the current is carried by a process of metallic conduction. The metallic nature of these alloys, moreover, is borne out by their appearance, which is distinctly that of a metal. It will be noted that at 500°, the resistance-composition diagram has an inflection point indicating that, at higher concentrations of sodium telluride, the resistance approaches a definite maximum value. This probably means that as the composition of the alloys approaches that of the normal telluride, Na_2Te, the conductance is more and more largely due to an electrolytic process: for pure sodium telluride is a normal type of salt and, doubtless, conducts according to an electrolytic process. In general, the order of magnitude of the resistance of mixtures containing larger percentages of sodium telluride corresponds to that of fused salts. As the temperature diminishes, the resistance of all the alloys increases markedly, but the curves are, in general, of much the same form.

There can be little doubt that in mixtures of sodium telluride and tellurium, we have an instance of mixed metallic and electrolytic conduction. The higher the percentage of tellurium, the more does the metallic overbalance the electrolytic process.

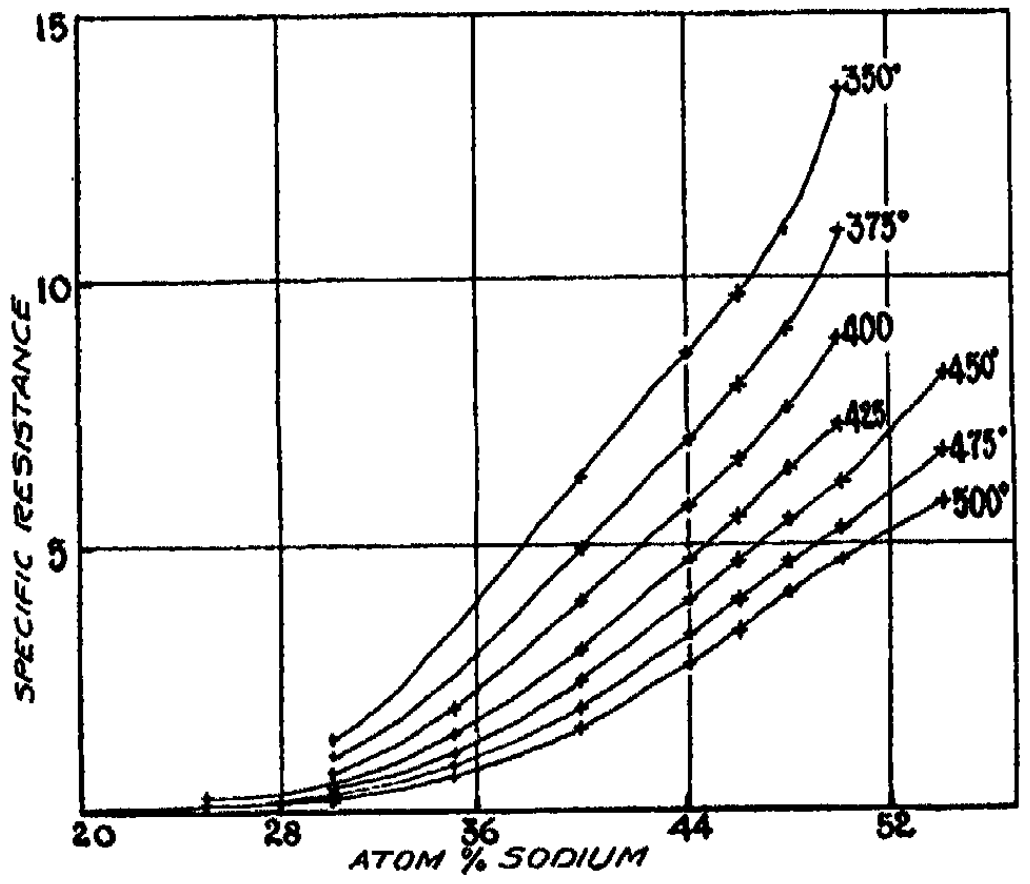

Fig. 5
Resistance of Alloys as a Function of Composition at Different Temperatures.

Summary

A method is described for preparing alloys of tellurium and sodium telluride of desired composition.

The resistance of liquid mixtures of tellurium and sodium telluride has been measured at various concentrations up to 54 atom % of sodium and at a series of temperatures up to 500°.

Mixtures rich in tellurium are good conductors and conduct metallicly. The conductance of mixtures rich in sodium telluride approximates that of fused salts and the conduction process is an electrolytic one.

Observations are recorded that indicate that sodium telluride and tellurium are completely miscible in the liquid state.

From the conductance-temperature curves, it may be inferred that sodium and tellurium form a compound, Na_2Te_6, having a congruent melting point at 436°.

The authors take pleasure in acknowledging their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant wherewith the precision bridge used in this investigation was purchased.

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LIQUID MIXTURES OF TELLURIUM AND SODIUM TELLURIDE
II. PHASE DIAGRAM OF THE SYSTEM Te-Na_2Te

BY CHARLES A. KRAUS AND STANLEY W. GLASS

As was stated in a preceding paper, Pellini and Quercigh[1] report a gap in the solubility curve of liquid mixtures of tellurium and sodium telluride at concentrations between approximately 25 and 37 atom % of sodium. Measurements of the electrical resistance of various liquid mixtures in this region, however, indicated complete miscibility of the two components. Accordingly, the phase diagram of this system was investigated in detail by the method of thermal analysis.

Materials, Apparatus and Method

Materials. The materials employed in the present investigation were the same as those used in connection with the conductance measurements reported in a preceding paper. The various alloys were made up in the same way and a detailed description of the method of preparation may, therefore, be omitted.

Apparatus. A known weight of the alloy prepared, as previously described, was introduced into a Pyrex tube having a diameter of approximately 30 mm. The lower end of this tube was drawn down to a slight taper in order to avoid the cracking of the tube when the alloy solidified. The thermocouple was located on the axis of the containing tube with its end approximately 15 mm. from the bottom. An atmosphere of nitrogen was maintained over the alloy at all times and the tube was provided with a stirring or shaking device for the purpose of facilitating crystallization. The tube containing the alloy was placed in a large graphite crucible, the intervening space being well lagged with Sil-o-Cel. The crucible, in turn, was placed in a large gas heated furnace provided with an insulating top.

The temperature-time curves were obtained by means of a thermocouple which was the same as that used in the preceding investigation, already referred to.

Method. The alloy was heated in the furnace to a temperature sufficiently high to insure complete fusion. In this condition it was thoroughly stirred, after which the furnace was shut down and the cooling curve was observed. The singular points on the cooling curves were noted and transferred to a composition-temperature diagram in the usual way. After obtaining a cooling curve, the alloy was remelted and the thermocouple removed. In certain instances, an alloy of higher tellurium content was then made up by adding a known additional weight of tellurium. The weight of alloy adhering to the thermocouple tube was determined and allowed for.

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[1] Pellini and Quercigh: Att. Accad. Lincei, (5), 19, II, 350 (1910).

The composition of the alloys was made up accurately to correspond to the compositions given (within 0.1%).

In the case of alloys containing more than 48 atom % of sodium, great difficulty was experienced in obtaining the point of initial appearance of the solid phase. In the earlier experiments, the results were so variable that all measurements between 50 and 54 atomic % of sodium, inclusive, were discarded and the results are not given below. A new series of measurements, however, was carried out within this region, the results for which are given. In these experiments, a larger containing tube was used and the amount of alloy was doubled, the mixtures were vigorously stirred and seeded with the expected solid phase. The results in this case were much more consistent than those previously obtained.

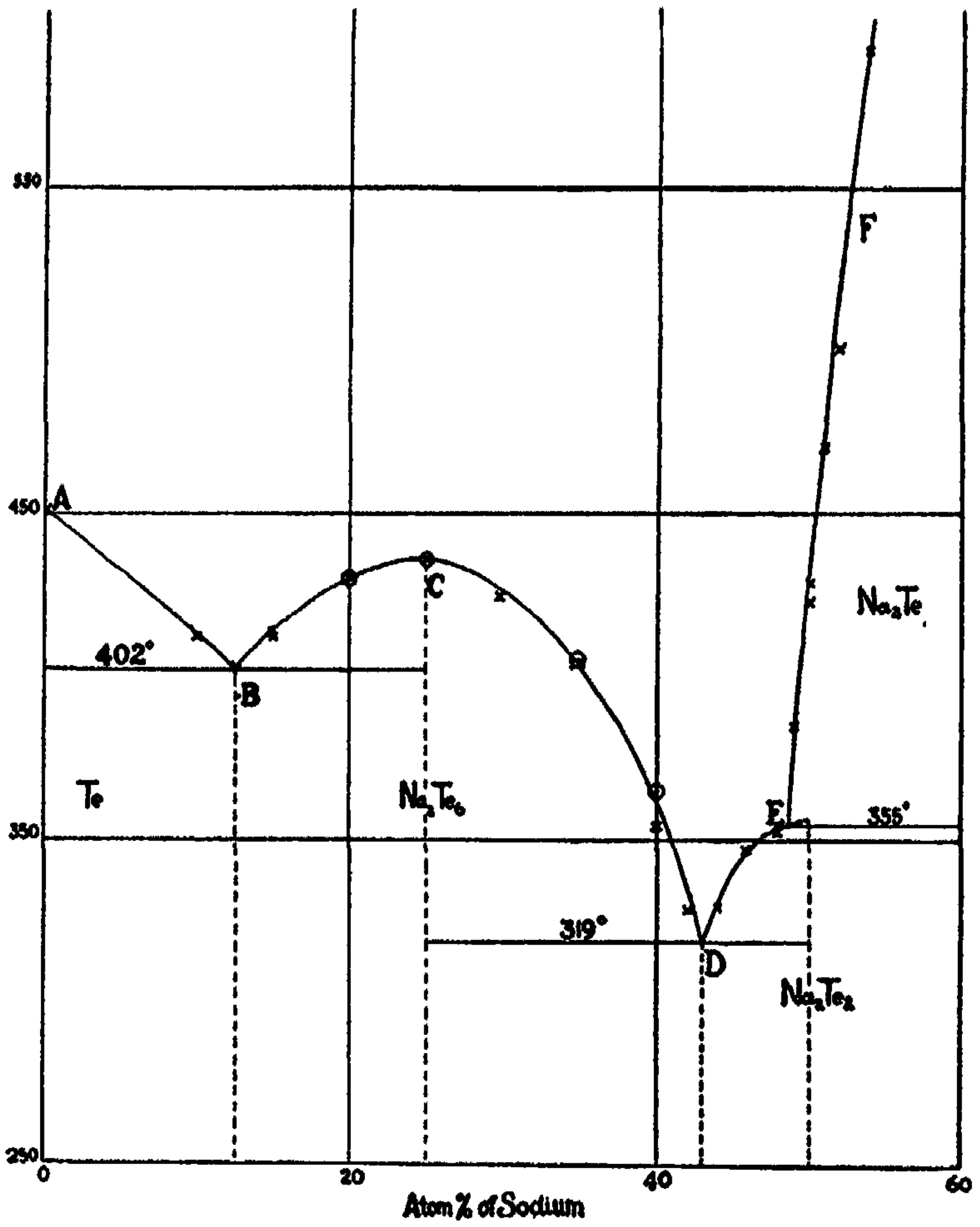

FIG. 1
Phase Diagram of the System Te-Na_2Te.

Experimental Data

The results obtained in the various experiments are summarized in the following table, where the number of the experiment is given in the first column, the atom % of sodium contained in the alloy in the second column, the temperature of initial appearance of solid phase in the third column, the eutectic point between the solid phases Te and Na_2Te_6 in the fourth column, the eutectic point between Na_2Te_6 and Na_2Te_2 in the fifth column, and the transition point between Na_2Te_2 and Na_2Te in the sixth column.

Data relating to Thermal Diagram of Te – Na_2Te

			Invariant Equilibria		
Exp. No.	Atom% Na	Begin. Cryst.	Eutectic Te+Na_2Te_6	Eutectic Na_2Te_6+Na_2Te_2	Transition Na_2Te_2−Na_2Te
	0	451.1	—	—	—
11	7.5	424.7	403.5	—	—
10	10	412.5	402.7	—	—
9	12.5	—	402.5	—	—
8	15	412.2	402.4	—	—
7	15	413.9	400.1	—	—
6	20	430.0	404.4	—	—
5	25	436.0	—	—	—
4	30	424.9	—	312.6	—
3	35	404.5	—	315.8	—
2	40	354.4	—	319.4	—
22	42	328.4	—	—	—
21	44	329.5	—	318.0	—
20	46	347.0	—	319.0	—
19	46	346.4	—	319.3	—
14	46	324.9	—	310.5	—
18a	48	352.3	—	319.2	—
18b	48	337.8	—	319.1	—
18c	48	351.0	—	—	—
30	49	385.0	—	303.0	353.0
31e	50	—	—	307.0	352.3
31d	50	—	—	—	354.9
31c	50	—	—	—	352.5
31b	50	429.1	—	303.0	351.5
31a	50	—	—	301.0	355.2
29	50	423.4	—	304.4	350.5
28	51	470.6	—	297.7	348.7
27	52	500.8	—	314.3	346.8
26b	54	592.5	—	310.3	352.9
26a	54	—	—	310.7	351.4

The results are shown graphically in the accompanying figure. All the observations obtained appear on this plot with the exception of the point of initial crystallization in the case of experiments Nos. 20 and 18b.

Discussion

As may be seen from the figure, sodium and tellurium form the compounds Na_2Te, Na_2Te_2 and Na_2Te_6. The melting point of the compound Na_2Te was not determined in the present investigation but follows from the earlier work of Pellini and Quercigh. The compound Na_2Te_6 has a congruent melting point at 436°, which agrees well with the value approximated earlier by means of the conductance method. At a temperature of 355°, there is a transition between the normal telluride Na_2Te and a higher telluride, which is almost certainly Na_2Te_2. An exact determination of the composition of this compound is not possible by the method of thermal analysis, although the general form of the curve indicates a compound of approximately this composition. Kraus and Chiu[1] have shown that, in liquid ammonia, solid sodium telluride is in equilibrium with a solution whose composition corresponds to the formula Na_2Te_2. It is highly improbable that compounds of the type Na_3Te_2, for example, are capable of existence. It is hardly to be doubted, therefore, that the compound Na_2Te_2 exists and is in equilibrium with the melt along the curve *DE*.

The diagram shows two eutectic points, one at a composition of 12.5 atom % of sodium at 402.5°, the solid phases being tellurium and Na_2Te_6. The second eutectic lies at a composition of 43 atom % of sodium and a temperature of 319°, the solid phases being Na_2Te_6 and Na_2Te_2.

Both the eutectic temperatures at *B* and *D* are well established but it may be mentioned that the temperature of the latter point was obtained readily, only in the case of alloys whose composition approximated that of the eutectic mixture. Mixtures containing more than 48 atom % of sodium, in general, gave eutectic temperatures somewhat too low.

The method of thermal analysis did not give entirely satisfactory results for the freezing point curve of alloys containing between 40 and 43 atom % of sodium. In these regions, the conductivity method yielded results that are more reliable. According to this method, the resistance of the liquid mixture is followed up as a function of the temperature until a solid phase appears, when an inflection point occurs without discontinuity in the resistance curve itself. If the appearance of the solid phase is suspended, the resistance curve of the liquid phase proceeds into the metastable region and, when a solid phase appears, a discontinuous change of resistance occurs, after which the resistance follows along the curve of the solid-liquid mixture. By extrapolating the curve of the solid-liquid mixture until it intersects that of the homogeneous liquid phase, the temperature at which the solid phase appears may be determined unambiguously. Data relating to the resistance-temperature curves of alloys containing 20, 25, 35 and 40 atom % of sodium are given in the previous paper. The temperatures obtained for the initial appearance of a solid phase are shown on the figure as circles. It will be seen that, at 40 atom % of sodium, the value obtained by the

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[1] Kraus and Chiu: J. Am. Chem. Soc., 44, 1999 (1922).

resistance method is about 10° higher than that obtained by the thermal method. It is believed that the former value is the more reliable and the curve in the figure is drawn accordingly. At 20, 25 and 35 atom % of sodium, the two methods are in excellent agreement.

The phase diagram, as determined by means of thermal analysis and resistance measurements, shows clearly that tellurium and sodium telluride are miscible in all proportions in the liquid phase. The gap in the miscibility curve, reported by Pellini and Quercigh, evidently does not exist.

It may be noted that, while the existence of the polytelluride Na_2Te_6 is well established according to the phase diagram, no evidence of this compound has been found in the study of solutions of the polytellurides in liquid ammonia. Kraus and Chiu have shown that the ditelluride, N_2Te_2, readily reacts with excess tellurium in liquid ammonia but the maximum tellurium content of the solution corresponds to the formula Na_2Te_4. The tellurium content increases with increasing concentration and it is possible that, in solution, there exists an equilibrium between Na_2Te_2 and Na_2Te_6.

Summary

The melting-point diagram of mixtures of tellurium and sodium telluride has been determined. The two components are completely miscible in the liquid phase.

In addition to the normal telluride, sodium and tellurium form two compounds, Na_2Te_2 and Na_2Te_6. The former has a transition point with the normal telluride at 355° and the latter a congruent melting point at 436°.

Eutectics are formed between Na_2Te_2 and Na_2Te_6 and between Na_2Te_6 and tellurium.

The results of the resistance method are in agreement with those of thermal analysis.

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STUDIES IN THE SOLUBILITIES OF THE SOLUBLE ELECTROLYTES

I. RELATIONSHIPS BETWEEN THE TEMPERATURE COEFFICIENTS*

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Various attempts have been made to formulate a theory of solubility of the soluble electrolytes and, although none is complete, they are all pretty much agreed on three determinant factors which we may describe as (1) cohesion of solute; (2) cohesion of solvent; and (3) adhesion of solvent and solute. In a number of recent papers, however, these cohesive and adhesive forces are treated, with very suggestive results, from the standpoint of modern atomic theory. It is the object of the present study to describe certain relationships which exist between the temperature coefficients of solubility and of which an interpretation in terms of these newer concepts appears possible. We shall therefore review briefly at the outset the more significant postulates respecting the above three factors.

We shall consider the ions of an electrolyte in the solid state to be arranged in a crystal lattice, their positions being controlled by electrostatic forces of attraction and repulsion. As a measure of the cohesion of the ions in this state we may take the lattice (free) energy, a characteristic constant which varies but little with temperature. In solution, we shall assume further, both cation and anion of a salt are able to attract by means of their electrostatic forces the dipolar water molecules. The magnitude of these forces of adhesion between solute and solvent is indicated approximately by the heats of hydration of the individual ions. Now, if the solubility of electrolytes is determined by the difference of these two energy factors, we should expect it to vary, qualitatively at least, with the heat of solution because this constant is equal to the heats of hydration of the ions minus the lattice energy of the salt. The possibility of such a relationship has been discussed by Butler.[1]

At this point a word may be said regarding one of the distinctions between soluble and insoluble electrolytes. As a general rule the soluble salts have relatively small heats of solution, which fact, according to Fiock and Rodebush,[2] means "that the electrical forces of an ion are neutralized to about the same extent in solution as in the crystal lattice." On the other hand the insoluble salts have somewhat larger, negative heats of solution, a condition which Fajans[3] has attributed to the abnormally large lattice energies which

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* Contribution from the Department of Chemistry of The Rice Institute.

[1] Butler: Z. physik. Chem., 113, 279 (1924).

[2] Fiock and Rodebush: J. Am. Chem. Soc., 48, 2522 (1926).

[3] Fajans: Z. Kristall., 61, 18 (1925); 66, 321 (1928).

result from the deformation in the solid state of the electronic shell of one ion under the influence of the electric field of the oppositely charged ion. In support of this argument, Herzfeld and Fischer[1] have shown for analogous insoluble salts that a salt is less soluble the more negative its heat of solution. Since we shall deal in the present paper only with the very soluble salts, it is safe to assume that we shall not meet with any pronounced effects of deformation. Nevertheless it must be remembered that deformation depends upon the particular properties of the constituent ions and that consequently the possibility of its existence cannot be disregarded.[2]

With respect to the hydration of ions we shall accept an additional postulate which was first proposed by Fajans[3] and which can be stated in the following form: When the number of molecules of water to be distributed between the ions of a salt is sufficiently limited, as in the saturated solutions of very soluble salts, the ensuing competition between the ions results in the stronger ion gaining control over these water molecules to the exclusion of the weaker ion. We shall hereafter refer to these ions, under the above conditions, as the dominant ion and the subordinate ion, respectively. To estimate the relative strengths of the ions of a salt we can employ either the free energies[4] of hydration of the gaseous ions or the heats[5] of hydration of the gaseous ions. The former is to be preferred.

On the grounds of these over-simplified postulates we may attempt to construct a picture of the saturated state, an equilibrium condition which is reached when the forces tending to unite the ions into a crystal lattice are balanced by the opposing forces tending to keep them in solution. The combining action, from our viewpoint, results from the forces of inter-ionic attraction which are probably independent of temperature. This variable factor will be indicated by Φ_{DX} where D and X represent the two ions involved. The action tending to keep the ions separated may be regarded as being composed of two different factors: (1) the thermal motion of the particles; and (2) the attraction between the dominant ion and the water dipoles. Both of these factors, it is obvious, must be dependent on temperature. By this sort of analysis we come, therefore, to the usual and plausible conclusion that it would be possible to represent the solubility of a salt by some general, complex function of Φ_{DX} and T.

But in this paper evidence will be adduced which can be taken to indicate that this function may be written in following less general form:

$$N_{DX} = \Phi_{DX} f_D (T) \qquad (1)$$

Here the solubility N_{DX} is expressed as the number of moles of water per mole of salt. The right hand member of the equation consists of two terms representing the opposing forces at the equilibrium state. Φ_{DX} is a constant para-

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[1] Herzfeld and Fischer: Z. Elektrochemie, 26, 460 (1922).

[2] See Fajans: "The Theory of Strong Electrolytes," The Faraday Society, page 408.

[3] Fajans: Naturwissenschaften, 9, 2 (1921).

[4] Webb: J. Am. Chem. Soc., 48, 2600 (1926).

[5] Fajans: Verh. deutsch. physik. Ges., 21, 549, 709 (1919).

meter, characteristic of the forces of inter-ionic attraction and $f_D(T)$ is an indefinite function which represents the variation of the two factors influenced by temperature. Now, although the precise nature of parameter and function is unknown, we can make the important assumption that the latter, at a given temperature, has the same value for all solutions with a common dominant ion D. For the two factors whose variation with temperature are described by $f_D(T)$ are, according to the dominant ion concept, identical under the above condition.

In support of the foregoing deduction we shall consider two relationships which can be deduced from equation (1). For a group of salts, DX, DY, etc., we have equations analogous to (1) which on differentiation with respect to temperature become:

$$\left(\frac{dN_{DX}}{dT}\right)_{T_1} = \Phi_{DX} f_D'(T_1) \tag{2a}$$

$$\left(\frac{dN_{DY}}{dT}\right)_{T_1} = \Phi_{DY} f_D'(T_1) \tag{2b}$$

Dividing (2a) by (2b) we obtain, since $f'_D(T)$ is identical because of the common dominant ion,

$$\frac{\left(\frac{dN_{DX}}{dT}\right)_{T_1}}{\left(\frac{dN_{DY}}{dT}\right)_{T_1}} = \frac{\Phi_{DX}}{\Phi_{DY}} = \text{constant} \tag{3}$$

In other words the ratio of the temperature coefficients of solubility at any given temperature of any two salts which fulfill the above conditions is independent of temperature.

In the second place, if the differentiation be carried out at a different temperature, say T_2, we obtain equations analogous to (2a) and (2b). They are

$$\left(\frac{dN_{DX}}{dT}\right)_{T_2} = \Phi_{DX} f_D'(T_2) \tag{4a}$$

$$\left(\frac{dN_{DY}}{dT}\right)_{T_2} = \Phi_{DY} f_D'(T_2) \tag{4b}$$

Now, dividing equation (2a) by (4a), and equation (2b) by (4b) we get

$$\frac{\left(\frac{dN_{DX}}{dT}\right)_{T_1}}{\left(\frac{dN_{DX}}{dT}\right)_{T_2}} = \frac{\left(\frac{dN_{DY}}{dT}\right)_{T_1}}{\left(\frac{dN_{DY}}{dT}\right)_{T_2}} = \frac{f_D'(T_1)}{f_D'(T_2)} = \text{const.} \tag{5}$$

This relationship means, of course, that the ratio of the temperature coefficient of solubility at one temperature to that at another temperature is identical for all salts with the same dominant ion.

In what follows we shall consider examples which appear to be in accord with these deductions. It will be recognized, to be sure, that the theory just outlined has been developed to make the empirical relationships intelligible. Nevertheless, it may be mentioned that certain conclusions, which this provisional theory suggests, have been tested and confirmed, and will be reported in some papers in the course of preparation.

The selection of typical examples, however, is a matter of considerable difficulty because of the requirements which they must satisfy. Thus, in any particular group of salts, each salt must have the same dominant ion and, besides, the solubilities of these salts must be sufficiently great (N small) to allow the dominant ion to come into exclusive control of the water dipoles. Moreover, there must be no change in the solid state, such as the formation of hydrates, which would affect the parameter Φ_{DX}. Although there are many groups of salts which meet the above conditions, our actual choice is seriously restricted by the fragmentary nature of the available solubility data.

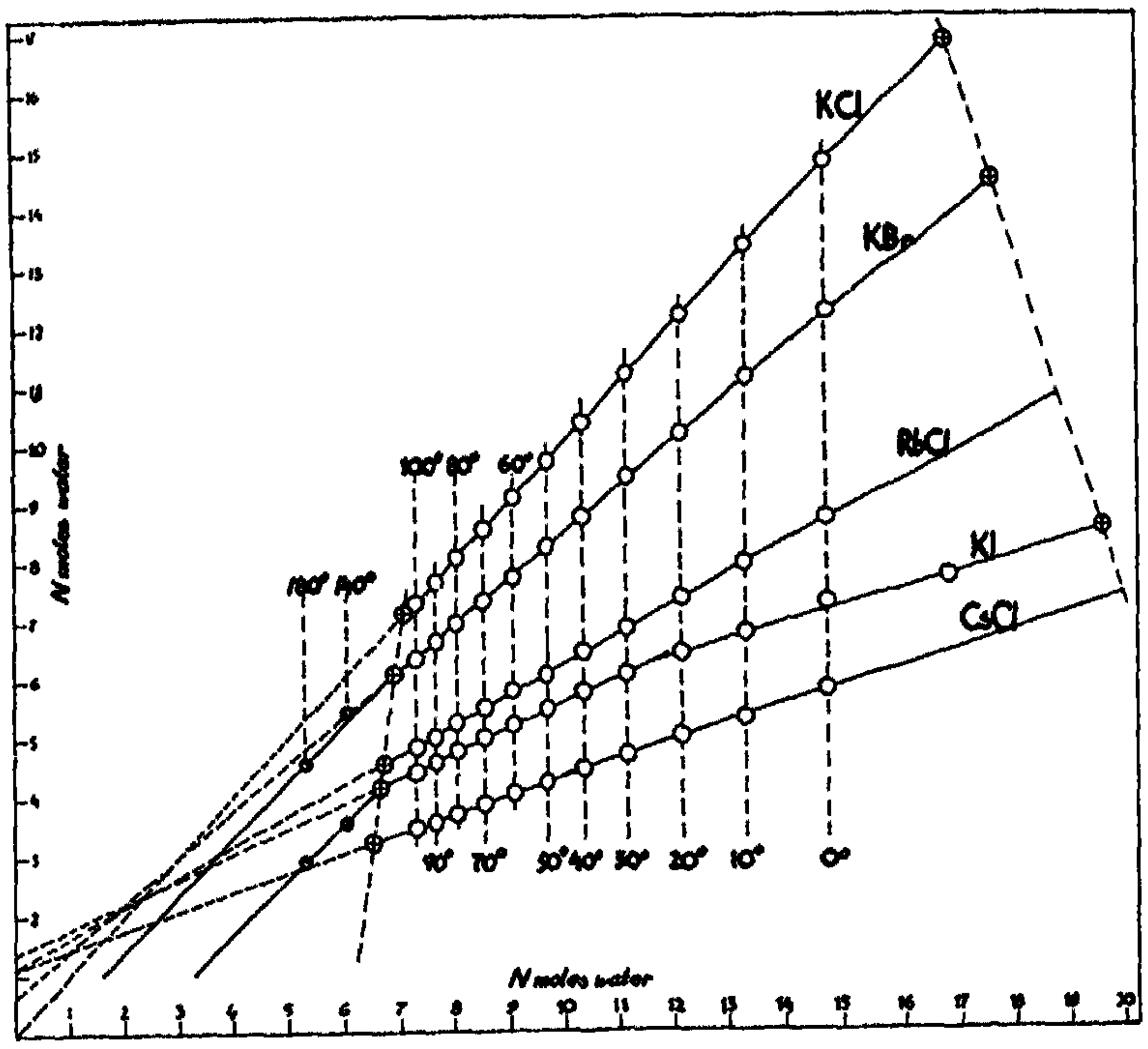

Fig. 1
N values of salts with common dominant ion plotted against N values of potassium chloride at corresponding temperatures.

Probably the simplest group of salts which we shall consider consists of the chloride, bromide, and iodide of potassium, where the potassium ion is undoubtedly dominant. It appears, further, that two other salts, the chlorides of rubidum and cesium, also belong in this group, despite the fact that, according to the free energies of hydration, the cation in both cases is slightly stronger than the chloride ion. They were included originally, however, because the chloride ion has a greater heat of hydration than the cations and would therefore be dominant. Moreover, it should be noted that both potassium and chloride ion have the same electronic structure and almost the same heats of hydration. In order to show to what extent these five salts satisfy the rule expressed by equation (3) we have plotted in Fig. 1 the N values of each salt against the N values of potassium chloride at the corresponding temperatures. The necessary data for the construction of this graph are contained in Table I.

TABLE I

Values* of N at Different Temperatures

T	KCl	KBr	RbCl	KI	CsCl
0°	14.79	12.22	8.72	7.30	5.80
10	13.37	11.12	7.96	6.78	5.36
20	12.18	10.15	7.37	6.41	5.02
30	11.18	9.36	6.83	6.06	4.74
40	10.35	8.75	6.48	5.77	4.49
50	9.72	8.24	6.14	5.49	4.27
60	9.10	7.74	5.81	5.24	4.07
70	8.57	7.34	5.52	5.00	3.90
80	8.19	6.96	5.28	4.80	3.74
90	7.66	6.67	5.04	4.60	3.59
100	7.31	6.36	4.84	4.43	3.46

* Landolt-Börnstein's Tabellen, 2nd edition, and The International Critical Tables are the sources of all solubility data employed in this paper.

A scrutiny of Fig. 1 shows that the plotted points of each salt all fall on straight lines which may be represented by the following general equation:

$$N^{T}_{DX} = aN^{T}_{KCl} + b \qquad (6)$$

The obvious breaks in the lines of potassium iodide and cesium chloride will be discussed later in this paper. The values of the constants a and b in the above equation have been determined for each of the four lines and are given below:

Line	a	b
KBr	0.783	0.636
RbCl	0.514	1.128
KI	0.279	3.022
	0.422	1.380
CsCl	0.290	1.496
	0.330	1.064

To ascertain how real these linear relationships are, N values have been calculated for different temperatures by means of these constants and the N values of potassium chloride. Only the differences between the computed and experimental values are given in Table II.

TABLE II

Differences between Calculated and Experimental Values of N

T	KBr	RbCl	KI	CsCl
0	−0.01	0.00	−0.14	−0.02
10	−0.02	0.04	−0.02	0.02
20	0.02	0.01	0.02	0.00
30	0.03	−0.01	0.04	−0.01
40	−0.01	−0.02	−0.02	0.00
50	0.00	−0.02	−0.01	0.00
60	0.02	−0.01	−0.02	0.00
70	0.00	0.01	0.00	−0.01
80	0.02	0.01	0.00	0.00
90	−0.04	0.02	0.01	0.00
100	0.00	0.03	0.04	0.01

It is clear from the figures given in this table that the linear relationships of equation (6) are satisfied well within the limits of experimental error.

We are now able to show that this group of salts satisfies the conditions of the rule which is expressed by equation (3) For, if we differentiate equation (6) with respect to temperature, we get the following expression:

$$\left(\frac{dN_{DX}}{dT}\right)_T = a\left(\frac{dN_{KCl}}{dT}\right)_T \qquad (7)$$

In other words the ratio of the temperature coefficients of solubility of any of the four salts at any given temperature between 0°C. and 100°C. to that of potassium chloride at the same temperature is equal to the characteristic constant a.

The possible interpretation of the extreme limits (under constant pressure) of saturated solutions—their freezing and boiling points—in terms of Fig. 1 is a matter of some interest. Since the argument is the same in both cases, we shall confine our attention to an examination of the conditions which obtain at the cryohydric point.

From the viewpoint of this paper we may say that the freezing point of pure water is reached when the thermal motion of the polar molecules is just offset by the electrostatic forces which tend to unite them into crystalline ice. The presence of an ion, however, by attracting the dipoles acts like the thermal motion to prevent combination into ice crystals. Since in effect it is equivalent to an increase of temperature, there must be a corresponding lowering of temperature before crystallization of ice can take place. The amount of this lowering would naturally depend on the extent of the influence of the ion. For saturated solutions involving a common dominant ion we might at first glance expect the above lowering ΔT to be proportional to the concentration of the dominant ion, that is, inversely proportional to N_c. In Table III some data are given which show clearly that this expectation[1] is only approximately fulfilled.

TABLE III

Data for the Cryohydric Points*

Salt	KCl	KBr	KI	NH_4Cl	NH_4I
N_c	16.82	14.47	8.541	6.44	10.67
ΔT	10.66	12.60	23.2	15.36	27.5
$N_c x \Delta T$	179.3	182.2	198.2	190.5	177.1

* Taken from the International Critical Tables.

The invalidity of the foregoing statement is the consequence of a particular, incorrect assumption; to wit, that the forces opposing the crystallization of ice, the thermal motion and the dominant ion-dipole attraction, are directly related to temperature. Indeed, the indefinite temperature function in equation (1) was supposed to represent this rather complex relationship. For this reason, therefore, we are justified in looking for a more precise relationship to exist between the N_c values at the cryohydric point and the corresponding values of the temperature function. Moreover, it follows from equation (1) that Fig. 1 may be used to depict this relationship. For the abscissa points are virtually values of the temperature function at the given temperatures multiplied by an arbitrary factor which in this instance is Φ_{KCl}. Therefore, when in Fig. 1 the cryohydric values N_c of the three salts are plotted on the appropriate lines, we can imagine them to be plotted against the corresponding values of the temperature function. These three points all fall on a straight line, from which fact it follows that N_c decreases linearly with an increase of the temperature function. The possibility of representing this cryohydric line by an equation analogous to equation (1) at once suggests itself. In such an equation the Φ term would represent the intermolecular crystallizing forces of the water molecules and N_c, the number of moles of water which can be held by the dominant ion at a given temperature in opposition to the above forces. The intersections of this line and the solubility lines in Fig. 1 become understandable when it is recalled that at the cryohydric point the crystallizing forces and the opposing agencies of both salt and ice must all be equal.

No further discussion of the matter is justifiable until more data are available. Even here our conclusion that the N_c points fall on a straight line assumes that the line for potassium iodide is correctly plotted. The following evidence, however, apparently verifies this assumption. First, the N value of potassium iodide at −10.66°C., the cryohydric temperature of potassium

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[1] Engel: Compt. rend., 117, 485 (1893). His statement of this conclusion as a rule without qualification is obviously incorrect.

chloride, is found by interpolation of Kremann and Kerschbaum's data to be 7.72. In the graph the point plotted for this figure falls squarely on the line. Second, the value of N at 0°C., calculated from the equation of the line, is 7.16 and it is approximately the mean of the measurements of Kremann and Kershbaum,[1] and van Dam and Donk,[2] who found 7.12 and 7.21 respectively.

The above considerations apply with equal force to the rise in boiling point of saturated solutions. Here, however, it is a question of increasing the temperature until the water dipoles are held no more firmly than they are in the pure solvent. Below in Table IV are listed the data employed in plotting the N_b values at the boiling points of the saturated solutions.

TABLE IV

Data for the Boiling Points of Saturated Solutions

Salt	KCl[3]	KBr[4]	KI[4]	RbCl[3]	CsCl[3]
N_b	7.12	12.0	4.2	4.58	3.22
ΔT	8.10	6.1	18.5	14.0	19.4
$N_b x \Delta T$	57	55	78	59	62

The solubilities of salts at temperatures above the boiling points of their solutions may also be dealt with from the standpoint of Fig. 1. On the assumption that the temperature function (equation 1) is unchanged under these conditions, we may indicate the variation of these supra-boiling point solubilities by the dotted lines. The curious coincidence of these lines at a point when N equals about 2.5 will be considered in connection with the next figure. We know, however, that these dotted lines are hypothetical because above the boiling point the temperature function must take into account a new variable, pressure. Nevertheless, if it is conceivable that the new form of the temperature function is the same for all salts with the same dominant ion, the high temperature solubilities can be plotted in the same manner as those of low temperature.

Unfortunately the only trustworthy measurements at high temperatures by which we can examine this matter are those of Tilden and Shenstone.[5] The use of their figures for the solubilities of the potassium halides is, moreover, restricted to the only two temperatures at which they determined the solubility of the bromide. The N values computed from their data are as follows:

T	KCl	KBr	KI
140°	6.07	5.46	3.56
180°	5.34	4.58	2.91

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[1] Kremann and Kershbaum: Z. anorg. Chem., 56, 218 (1907).

[2] van Dam and Donk: Chem. Weekblad, 8, 848 (1911).

[3] Berkeley: Phil. Trans., 203A, 208 (1904).

[4] Extrapolated from data in Landolt-Börnstein's Tabellen, 2nd. edition.

[5] Tilden and Shenstone: Phil. Trans., 175, 23 (1884).

Points for these values are plotted in Fig. 1 as solid dots. Since the boiling point of the saturated solution would presumably be the lower limit of the new temperature function, lines for the high temperature solubilities are drawn so as to pass through these limiting points. Further justification of this rather arbitrary method of drawing the lines will be shown in a discussion of the next figure. However, if the lines are drawn correctly, we have the interesting conclusion, indicated by the parallel lines with a slope almost equal to one, that above their boiling points the temperature coefficients of solubility of these three salts are sensibly identical.

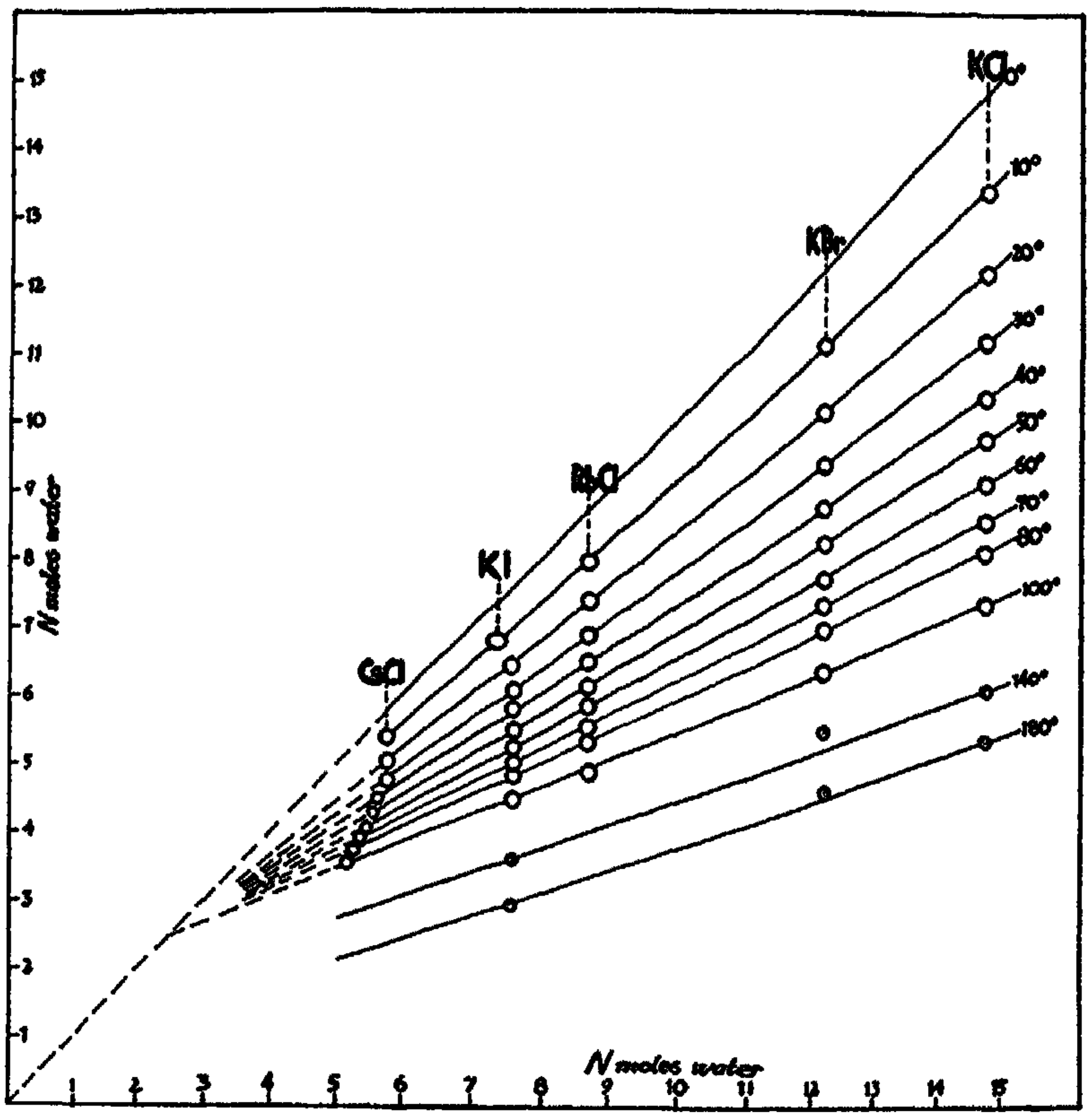

FIG. 2
N values of salts at various temperatures plotted against N values of same salts at 0°C.

To test the second rule regarding temperature coefficients, which is expressed by equation (5), we shall plot (Fig. 2) the N values of each salt at indicated temperatures against its N value at 0°C. The plotted points yield straight lines, although two of them, those of potassium iodide and cesium chloride are again broken. These lines can be represented by the linear expression

$$N^{T}_{DX} = a\,N^{o}_{DX} + b \qquad (8)$$

which on differentiation with respect to temperature gives the expected relationship between the temperature coefficients of solubility. The constant a is obviously independent of the salts involved.

A few interesting features of this figure may be mentioned. First, it will be noted that the lines, if projected, intersect at a point, when N equals 2.5, which may be taken to represent a hypothetical substance whose solubility is independent of temperature. Since the abscissa points really represent the Φ function in arbitrary units, it can be seen that the nature of this hypothetical substance could be estimated, if we had some fundamental ionic property proportional to Φ. Some of the possible properties have been tested and of these, the ionic ratio[1] is particularly suggestive. For when the N^T_{KX} values of the potassium halides are plotted against the corresponding value of the ratio r_X/r_K of the ionic radii, the isotherms are straight lines intersecting at a point when N is approximately 2.5. The value of the ratio at this junction is about 1.85, which would give the hypothetical anion a radius of about 2.46 Å. The rubidium and cesium salts, however, give an entirely different value. The interpretation to be placed on this hypothetical substance is made still more difficult by the evidence in Fig. 1 that all of these salts at a sufficiently high temperature have almost this same solubility. A possible conjecture is that N equal to 2.5 represents a constant hydration factor of the dominant ion.

In Fig. 2 are also included lines for the two temperatures above the boiling points for which data are available. The three points for 180°C, fall almost on a straight line. The line for 140°C., however, is drawn through two points on the plausible assumption that the solubility measurements of the bromide are least precise. Speculation regarding the significance of these lines is pointless because of the meagreness of the data. We may only observe that the slopes of the lines as drawn are practically equal and do not differ greatly from that of the 100°C. line.

According to our argument the linear relationships portrayed in Figs. 1 and 2 should not be peculiar to the group of salts considered but should be obtained with any salt containing potassium or chloride ion as the dominant ion. It is this condition, however, which limits the number of possible salts because these two ions are relatively weak. As a matter of fact the N values of twelve potassium salts were plotted against the N values of potassium chloride as in Fig. 1 and only in a few cases (chromate, nitrite, formate, selenate) did the plotted points appear to fall on a straight line. But even here the conclusion was equivocal. The number of possible chlorides is, on theoretical grounds, practically restricted to the two salts which we have considered. The N values of the only other salt, ammonium chloride, do not give a straight line when plotted in Fig. 1.

From this last statement we may conclude therefore that the ammonium ion is dominant in the chloride and consequently also in the bromide and iodide, a conclusion which is susceptible to the same method of testing em-

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[1] Pauling: J. Am. Chem. Soc., 49, 765 (1927).

ployed in Figs. 1 and 2. That it is doubtless correct is shown by Fig. 3 where the N values of the bromide and iodide are plotted against those of the chloride at corresponding temperatures. The data to accompany Fig. 3 are contained in Table V.

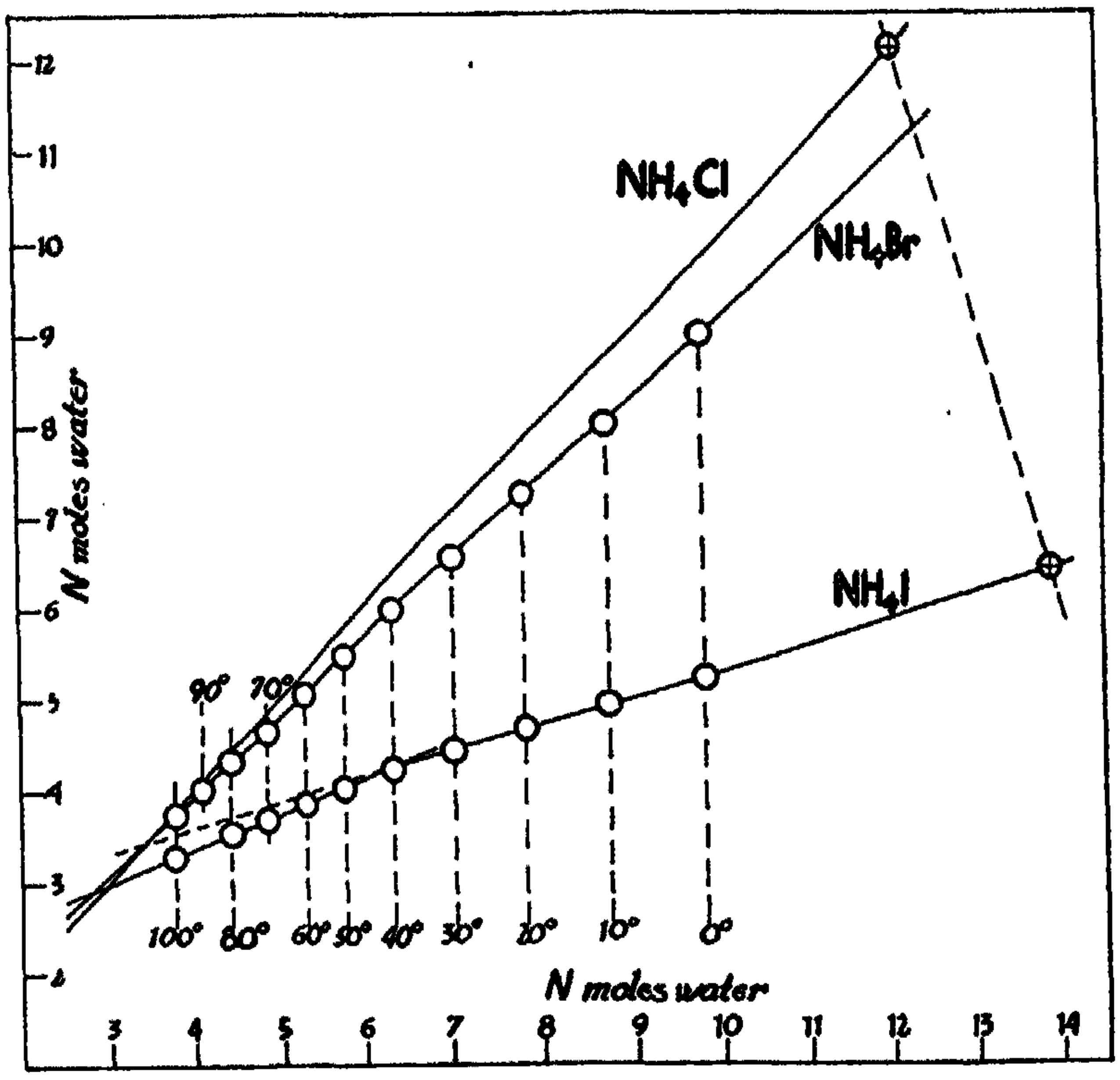

FIG. 3
N values of ammonium bromide and iodide plotted against N values of ammonium chloride at corresponding temperatures.

TABLE V

N Values of the Ammonium Salts

Salt	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
NH_4Cl	9.81	8.74	7.84	7.03	6.37	5.78	5.27	4.84	4.44	4.10	3.77
NH_4Br	8.98	8.00	7.21	6.54	5.97	5.48	5.05	4.66	4.31	4.01	3.74
NH_4I	5.22	4.93	4.67	4.44	4.23	4.03	3.85	3.68	3.52		3.29

Many features of this diagram are clearly analogous to those of Fig. 1 and need no additional discussion. It may be recalled at this point, however, that the constant a (equation 6) represents the ratio of the Φ factors of the different halides to that of the chloride. Therefore, in view of the usual assumption that the ammonium and potassium ions are very similar, we should expect this similarity to be reflected in the corresponding values of this constant a. The comparison of these constants, given in the subjoined table, have consequently an interesting bearing on the interpretation of equation (1).

Line.	Chloride	Bromide	Iodide		Cryohydric
K^+	1.0	0.783	0.279	0.422	−3.0
NH_4^+	1.0	0.860	0.287	0.376	−3.2
Ratio	1.0	0.91	0.97	1.1	0.94

The data for the cryohydric points are given in Table III. It is necessary to record, however, that Smith and Eastlack[1] look upon Guthrie's determination of this constant of the iodide, which is the one given in the table, as extremely inaccurate.

The final group of salts with a dominant cation which we shall consider are the strontium halides. This group is of particular interest because the salts in the solid state are hydrated over the entire temperature range. At high temperatures they are all hexahydrates and at low temperatures, dihydrates. Their respective transition temperatures are given below:

$SrCl_2$	$SrBr_2$	SrI_2
61.34°	88.6°	84° (?)

The N values of these salts are given in Table VI.

TABLE VI

N Values of the Strontium Halides

T	$SrCl_2$	$SrBr_2$	SrI_2
−10°	21.5	17.2	11.8
0	19.8	16.0	11.3
10	18.2	14.9	10.9
20	16.7	13.9	10.5
30	15.0	12.9	10.1
40	13.4	11.9	9.6
50	11.9	11.1	9.3
60	10.6	10.2	9.7
70	10.0	9.3	8.1
80	9.5	8.0	7.1
90	9.1	6.5	——
100	8.8	6.2	5.3
Transition	10.4	6.50	5.97

In Fig. 4 the N values of the bromide and iodide are plotted against those of the chloride; the transition points are indicated by solid dots. The analysis of the figure will be omitted since it is analogous to that employed in connection with Figs. 1 and 3. Several interesting features of the figure, however, will be mentioned. Thus it can be seen that the projections of the low-

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[1] Smith and Eastlack: J. Am. Chem. Soc., 38, 1500 (1916).

temperature, hexahydrate lines intersect when their N values are approximately 8.8. Curiously enough, if we subtract the six moles of water which go into the crystalline state, we get a quantity very nearly the same as that obtained in Figs. 1 and 2 for the hypothetical potassium salts. By an extrapolation of the solubility curve of the chloride it is found that this hypothetical point would be reached at a temperature of about 80°C. Now, if we plot the true N values of the bromide and iodide at this temperature against an abscissa value of 8.2, we find that they do not fall on the proper lines. This fact means that the breaks in the bromide and iodide lines at approximately the transition point of the chloride are not due entirely to a discontinuity in the sequence of the abscissa points. Or, in other words, we have a coincidence of two discontinuities, one in the bromide and iodide lines, and one in the abscissa points. As a consequence the resultant break in these two lines is greater than any we have met with heretofore. Although the solubility measurements above 60°C. are sufficiently precise to justify the above conclusion, they do not warrant further speculation.

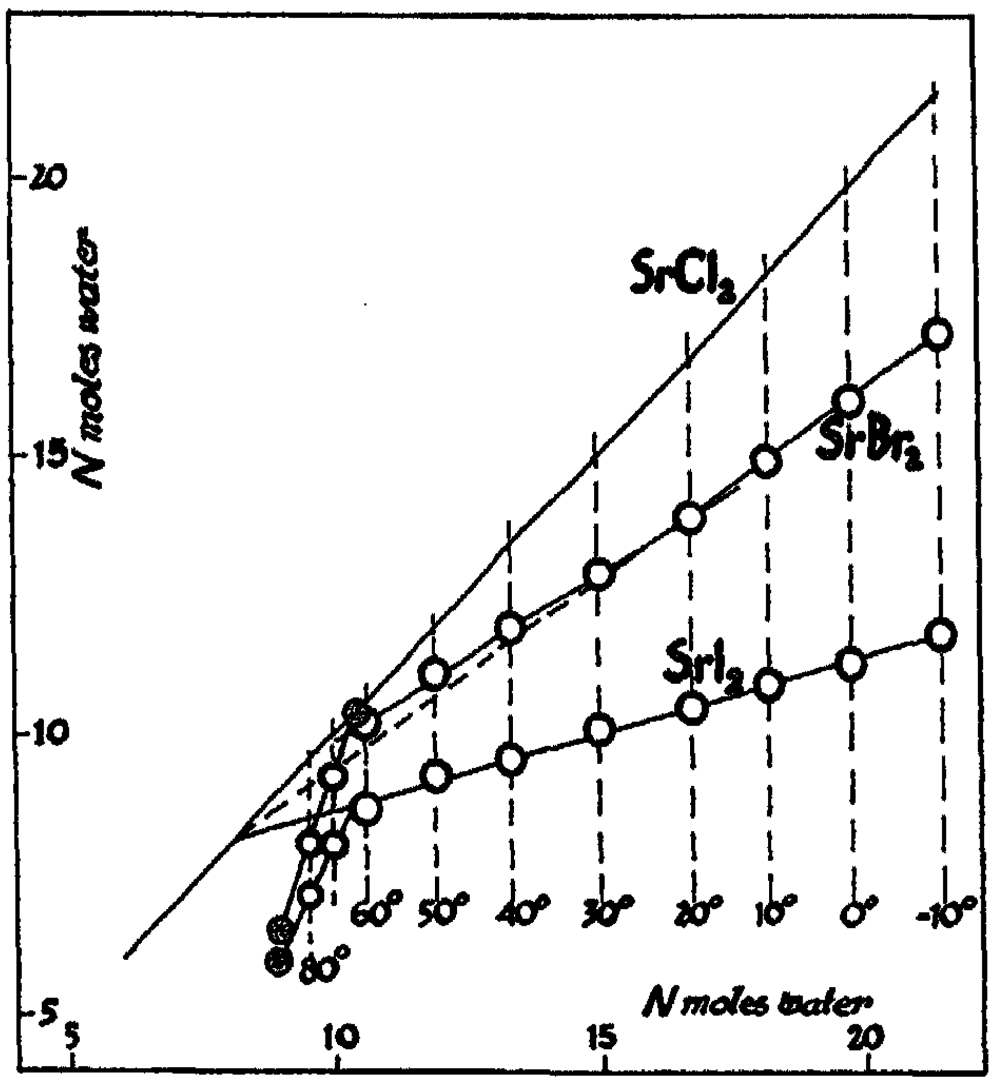

Fig. 4
N values of strontium bromide and iodide plotted against N values of strontium chloride at corresponding temperatures.

In addition to the above examples other salts have been examined by the same method and, so far as the fragmentary data permit decision, they are not out of harmony with the conclusions of the present study. This statement applies to such cases as sulfates and nitrates, where the anion is dominant, as well as to other salts with dominant cations. Some of these examples will be taken up in subsequent papers.

In conclusion we may touch on the subject of the breaks which occur in some of the plotted lines of the diagrams presented in this paper. In the first place it should be noted that these breaks correspond to real discontinuities in the usual solubility curves which bear, in many respects, remarkably close resemblance to the familiar discontinuities at the transition points of hydrates. Indeed, it is only because they are not so sharply defined in the customary method of plotting that they have hitherto not been recognized. The breaks under discussion must, according to the argument which has been advanced, arise from a discontinuity either in the Φ or the temperature function (equation 1). But it is not possible at this time to distinguish definitely between these alternatives. There is some evidence, however, which lends itself to the assumption that it is the Φ function which suffers a discontinuity because of some alteration in the property of the subordinate ion. Thus we find that in practically every instance the breaks in the lines occur only when the subordinate ion is relatively very weak.

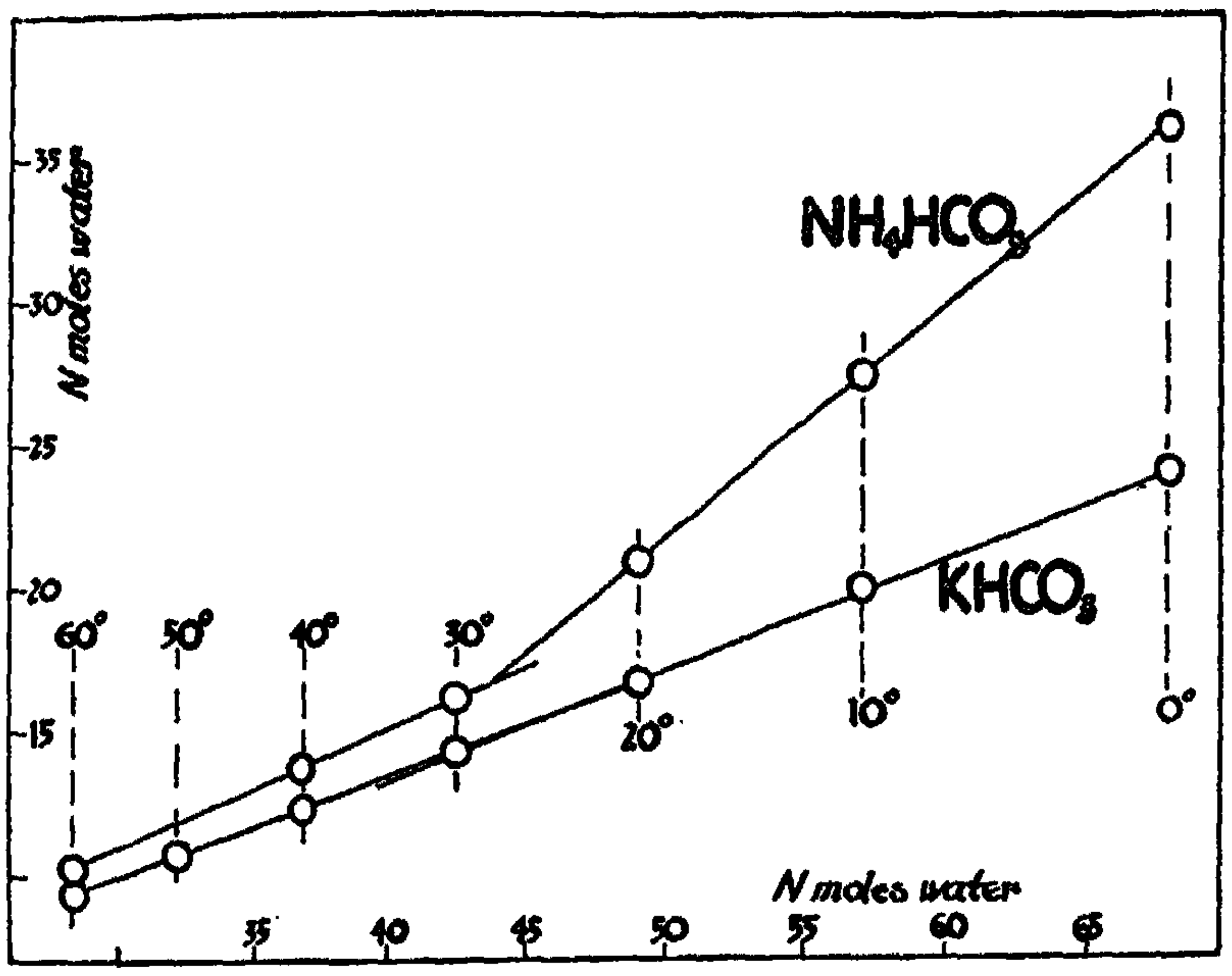

Fig. 5

N values of potassium and ammonium bicarbonate plotted against N values of sodium bicarbonate at corresponding temperatures.

Even stronger evidence in favor of this viewpoint can be found in Fig. 5, for which the essential data are contained in Table VII. Here we have plotted N values of the potassium and ammonium salts against the corresponding N values of sodium bicarbonate, and we may take the resulting straight lines to indicate that the anion is dominant. Nevertheless both lines exhibit discontinuities. Now, when it is recalled that the ammonium ion is very similar to the potassium ion, we should expect the Φ function of both salts to be nearly alike and, consequently, the slopes of both lines to be almost the same. It will be noted, however, that this condition obtains only at high temperatures while below the transition temperature the slopes of the lines are markedly different. This particular break would be understandable if one could attribute it to a change in the subordinate ammonium ion.

TABLE VII

N Values of the N Bicarbonate Salts

	0°	10°	20°	30°	40°	50°	60°
$NaHCO_3$	68.0	57.0	49.0	42.5	36.8	32.1	28.4
$KHCO_3$	24.0	20.0	16.7	14.3	12.3	10.7	9.3
NH_4HCO_3	37.1	27.5	20.9	16.2	13.7	——	10.2

But these suggestions regarding the origin of the discontinuities are by no means conclusive. For other factors such as relationships between the slopes of the broken lines and also relationships between the temperatures at which the breaks occur, must be taken into account. It is planned to discuss this aspect of the problem in another article for which the results of some significant experiments now in progress, will be available.

Summary

The present paper is to be considered a preliminary study of the problem of the solubility of the soluble electrolytes. In particular, certain relationships between the temperature coefficients of solubility are pointed out and an attempt is made to develop an outline of a theory which will explain these relationships.

As a consequence of the examination of the solubility curves, a number of discontinuities are discovered which heretofore have not been recognized. The possible significance of these discontinuities is discussed briefly from the standpoint of the present theory.

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Houston, Texas.

THE MUTUAL SALTING-OUT OF IONS

BY J. A. V. BUTLER

Introduction

In the original form of the Debye-Hückel theory of strong electrolytes the solvent enters only as the medium, having a certain dielectric constant, through which the electric forces between the ions act. In Debye's first calculation[1] the matter is treated as a question of the distribution of charged bodies in the electrostatic field around a charged sphere, in a medium of fixed dielectric constant. The rate of variation of the electric potential at a point in the vicinity of an ion is obtained by the use of Poisson's equation

$$\nabla^2\psi = \frac{4\pi\rho}{D} \tag{1}$$

where ρ is the electric density at that point. ρ is obtained by applying the Boltzmann equation to the distribution of ions in the electric field. The work done in bringing an ion of charge e to a point where the electric potential is ψ is $w = e\,\psi$ and if n° be the concentration of ions where $\psi = 0$, the concentration at potential ψ is

$$n = n^\circ e^{-\frac{\psi e}{kT}} \tag{2}$$

Thus the electric density at the given point, due to all the ions present, is

$$\rho = \Sigma n_i e_i = \Sigma n^\circ_i\, e_i\, e^{-\frac{\psi e_i}{kT}}$$

which to a first approximation reduces to

$$\rho = \frac{\Sigma n^\circ_i\, e_i^2}{kT}\,.\,\psi$$

Thus Debye obtained the equation

$$\nabla^2\psi = -\frac{4\pi}{D}\,\frac{\Sigma\, n^\circ_i\, e^2}{kT}\,.\,\psi \tag{3}$$

the solution of which enabled him to evaluate the potential at the surface of an ion due to the "ion atmosphere," and thence the electric work done, on account of interionic forces, in giving the ion its charge. In this way he obtained the expression

$$\log f = -A\sqrt{\mu} \tag{4}$$

or taking into account the radius of the ion

$$\log f = -\frac{A\sqrt{\mu}}{1 + C\sqrt{\mu}} \tag{4a}$$

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[1] Physik. Z., 25, 97 (1924).

where $\mu = \Sigma m_i z_i^2$ (m_i = ion concentration, z_i = valency of ion) and A and C are constants (C depending on the supposed ionic radius). This equation agrees excellently with the activity coefficients of ions at very small concentrations, and A calculated from absolute constants agrees with the observed figures, but it cannot account for the rise of activity coefficients in concentrated solutions.

In his attempt to extend the theory to concentrated solutions, Hückel[1] discussed at some length the effect of the electric field of the ions on the solvent molecules and pointed out that polarizable molecules tend to congregate round an ion where the electric field is strongest, displacing to a certain extent the other ions in its vicinity.[1] Hückel considered that the effect of this behaviour was obtained by introducing the "phenomenological law that the dielectric constant of the solution diminishes with increasing electrolyte concentration." In this way he obtained an additional term, linear with respect to the concentration; giving the equation the complete form:

$$\log f = -\frac{A\sqrt{\mu}}{1 + C\sqrt{\mu}} + B\mu \qquad (5)$$

where B is related to the dielectric constant lowering produced by the electrolyte. This equation is in accordance with the type of empirical equation required to fit the observed activity coefficients, but it is doubtful whether the values of B given by the experimental data correspond with the actual dielectric constant lowerings of solutions.[2]

It is evident that if the molecules of the solvent are themselves attracted into the vicinity of the ion, $e\psi$ no longer correctly represents the work done by an ion in reaching a place where the potential is ψ. We may evaluate the correction required by making use of the result obtained in electrostatic theory,[3] that the work done by an element of dielectric of volume δv in moving from a position where the electric field is zero, to one in which the field is strength E and the polarization produced per unit P is

$$\delta v \int P dE = \frac{\alpha . E^2}{2} . \delta v,$$

assuming proportionality between P and E, i.e. $P = \alpha E$, where, in electrostatic theory $\alpha = \frac{\epsilon - 1}{4\pi}$ and ϵ corresponds to the "dielectric constant" of the element of material.

When an ion is brought from a distant point into the vicinity of a given ion it displaces an equal volume of the solvent in the opposite direction, and

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[1] Physik. Z., 26, 93 (1925).

[2] Cf. Harned: J. Am. Chem. Soc., 48, 326 (1926).

[3] Cf. G. H. Livens: "Theory of Electricity," 2nd Ed. (1926).

the work required to effect the transfer is equal to the difference between that required to remove the solvent molecules and that yielded on bringing up the ion. Thus we have

$$w' = \frac{\alpha' - \alpha''}{2} \,.\, E^2\,\delta v$$

where α' and α'' are the values of α for the solvent molecules and for the ion, respectively.

The total work done by the ion in reaching the given point is thus:

$$w = e\psi + \frac{\alpha' - \alpha''}{2} \,.\, E^2\,\delta v$$

so that (2) is replaced by

$$n = n_0 e^{-\left(\frac{\psi e}{kT} + \frac{\alpha' - \alpha''}{2kT} \cdot E^2.\delta v\right)}$$

and (3) becomes

$$\nabla^2\psi = 4\,\pi \Sigma e_i n^\circ_i e^{-\left(\frac{\psi e}{kT} + \frac{\alpha' - \alpha''}{2kT} \cdot E^2.\delta v\right)}$$

or to the first approximation

$$\nabla^2\psi = \frac{4\pi}{kT}\,\Sigma e_i^2 n_i^\circ \,.\, \psi e^{-\frac{\alpha' - \alpha''}{2kT} \cdot E^2.\delta v}$$

$$= \kappa^2\,\psi\, e^{-\lambda(\nabla\psi)^2} \qquad (6)$$

where $$\kappa^2 = \frac{4\pi}{kT}\,\Sigma e_i^2\, n_i^\circ$$

and $$\lambda = \frac{(\alpha' - \alpha'')\delta v}{2kT}$$

It is not possible to obtain a direct solution of (6) and a solution by means of approximations appears to be so complicated that its application to an actual case would be extremely difficult. Accordingly a cruder method of attacking the problem has been explored. An attempt is made to calculate separately the displacement of ions round a given ion due to the effect of the electric field on the solvent molecules, and to estimate its influence on the activity coefficient of the solution. Such a treatment cannot hope to give a quantitative solution of the problem, for in dealing with the simultaneous action of two forces, we cannot properly isolate each singly and obtain the total effect by summation. Nevertheless, in the absence of a better approach this treatment may indicate whether the effect is of prime or only secondary importance. We will consider first the distribution of two kinds of neutral molecules in the field of force surrounding an ion.

The Salting-out Effect

Consider an ion of charge e and radius a in a medium containing two kinds of molecules A and B. Let A be the solvent and B the dissolved substance, which is supposed to be present in comparatively small amount. If the dielectric constant of the solution is D the potential ψ at a distance r from the ion is

$$\psi = e/Dr$$

and the field strength

$$E = d\psi/dr = -\frac{e}{Dr^2}$$

The work done by electric forces in brinigng a molecule B from infinity to a distance r from the ion is thus

$$\int P_B.\delta v_B.dE = \frac{\alpha_B}{2} E^2.\,\delta v_B = \frac{\alpha_B e^2}{2D^2r^4}.\delta v_B$$

where

$$P_B = \alpha_B E.$$

When a molecule of volume δv_B is brought up to the given position an equal volume of the solvent A is displaced in the opposite direction and the work done against electric forces in this process is similarly

$$\frac{\alpha_A e^2}{2D^2r^4}\,.\,\delta v_B.$$

The total work done in effecting the transfer is thus:

$$w = (\alpha_A - \alpha_B)\frac{e^2}{2D^2r^4}\,.\,\delta v_B$$

and if n_B° be the concentration of B in the bulk of the liquid, that at a distance r from the ion

$$n_B = n_B^\circ\, e^{-\frac{\alpha_A - \alpha_B}{kT}\cdot\frac{e^2}{2D^2r^4}\cdot\delta v_B} \qquad (7)$$

Thus if the molecule A is more polarizable than B ($\alpha_A > \alpha_B$) the concentration of the latter is reduced in the vicinity of the ion *i.e.* it is salted out.

To a first approximation (7) may be written

$$n_B^\circ - n_B = n_B^\circ\left(\frac{\alpha_A - \alpha_B}{kT}\cdot\frac{e^2}{2D^2r^4}.\delta v_B\right),$$

a quantity which represents the deficit in the number of molecules of B per unit volume at a distance *r* from the ion, compared with their concentration in the bulk of the solution. The total deficit in the amount of B or the amount salted out by a single ion is thus

$$\Gamma_B = \int_a^\infty (n_B{}^\circ - n_B)\, 4\pi r^2 \,.\, dr$$

$$= n_B^\circ \int_a^\infty \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{e^2}{2D^2 r^4} \,.\, \delta v_B \,.\, 4\pi\, r \,.\, dr$$

$$= n_o{}^B \,.\, \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{4\pi\, \delta v_B}{2D^2} \cdot \frac{e^2}{a} \tag{8}$$

Now if the solution contains m_1 gram ions of charge e_1, m_2 gram ions of charge e_2, etc. per litre, the number of molecules of B salted out per cubic centimetre of solution is

$$\Gamma_B = n_B^\circ \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{4\pi\, \delta v_B}{2D^2} \sum \frac{e_1{}^2\, m_1}{a_1} \cdot \frac{N}{1000} \tag{8a}$$

Now if we suppose that the solution in the first place was saturated with B and contained S_o molecules per c.c., and that after the addition of the electrolyte contained S molecules per c.c.; $S = n_o$ and $S_o - S = \Gamma_B$ and the activity coefficient of the substance B in the electrolyte solution is

$$f = S_o/S$$

Thus we have

$$\log f = \log (S_o/S) = \log \left(1 + \frac{S_o - S}{S}\right) \approx \frac{S_o - S}{S} = \frac{\Gamma_B}{n_o},$$

making use of the approximation $\log (1 + x) = x$, which may be used legitimately so long as $\frac{S_o - S}{S}$ is small compared with one. Therefore under these conditions we may put

$$\log f = \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{4\pi\, \delta v_B}{2D^2} \cdot \sum \frac{e_1{}^2\, m_1}{a_1} \cdot \frac{N}{1000}$$

$$= \frac{(\alpha_A - \alpha_B)\delta v_B}{kT} \cdot \frac{4\pi \,.\, \epsilon_o{}^2\, N}{2000\; D^2} \cdot \sum \frac{\nu_1{}^2\; m_1}{a_1} \tag{9}$$

where r_1 is the valency of the ion (1) and ϵ_o is the charge on the electron.

This equation (10) is equivalent to one obtained by Debye and McAulay,[1] by making use of the principle that the electric energy in the dielectric in the region round the ion must tend to a minimum. The result given by these authors is

$$\log f = \lambda\, n' \frac{\Sigma\, \nu_1\; z_1{}^2\, \epsilon_o{}^2}{2 D_o a k T} \tag{10}$$

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[1] Physik. Z., 26, 22 (1925).

where n′ is the number of molecules of the salt per cubic centimetre and λ is defined by the relation $D = D_0(1 - \lambda n)$ where D is the dielectric constant of a solution containing n molecules of non-electrolyte per cubic centimetre. In (9) $4\pi(\alpha_A - \alpha_B)$ is the difference between the dielectric constants of molecules A and B. $4\pi(\alpha_A - \alpha_B)\,\delta v_B$ is the lowering of the dielectric constant produced by one molecule of B in a cubic centimetre of the solution so that

$$D = D_0 - 4\pi(\alpha_A - \alpha_B)\,\delta v_B . n$$

Thus

$$\lambda = \frac{4\pi(\alpha_A - \alpha_B)\,\delta v_B}{D_0}$$

and except for the fact that in (9) D is the dielectric constant of the solution and in (10) D_0 is the dielectric constant of the pure solvent, the two equations become identical.

The experimental data have been examined from the point of view of Debye's equation by M. Randall and C. F. Fairley[1] who come to the conclusion that "there seems to be a qualitative agreement with these demands [of the equation] in most cases, but not a quantitative one."

The derivation of the equation which has been given is both simpler than Debye's and is more closely connected with the physical mechanism of the process. Debye[2] in a more recent paper has given a more precise mathematical treatment in which the higher terms in the approximation (7a) are not neglected. The computation of the effect by integration by series is somewhat complicated and for our present purpose of exploration the simple form will suffice.

The Mutual Salting-out of Ions

The ions of a salt mutually affect each other in two ways: (1) by the forces between their electric charges, whereby they attract ions of opposite sign and repel ions of the same sign; (2) indirectly through the effect of their electric fields on the molecules of the solvent. In a polar solvent the molecules of the solvent tend to congregate round the ions thereby displacing or "salting-out" other ions. A complete theory of solutions of strong electrolytes must simultaneously take account of the forces arising from both these effects and calculate the distribution of ions round a given ion resulting therefrom. The mathematical difficulties of such a treatment have already been mentioned. We shall therefore suppose that the treatment of Debye and Hückel takes care of the effects arising from the specific forces between ions, and attempt to estimate separately the salting-out effect.

Making use of (8) the total number of ions of kind (1) salted out by a single given ion of charge e_1 and radius a_1 is

$$\Gamma_1 = n_1 \frac{\alpha_A - \alpha_1}{kT} \cdot \frac{4\pi\,\delta v_1}{2D^2} \cdot \frac{e_1^2}{a_1}$$

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[1] Chem. Reviews, 4, 271, 285 (1927).

[2] Z. physik. Chem., 130, 56 (1927).

Thus if the solution contains m_1 gram-ions of charge e_1, m_2 gram-ions of charge e_2, etc. per litre (where $n_1 = \frac{N}{1000} . m_1$, etc.), the number of ions of kind (1) salted out per cubic centimetre is

$$\Gamma_1 = n_1 \frac{\alpha_A - \alpha_1}{kT} \cdot \frac{4\pi\delta v_1}{2D^2} \cdot \frac{N\epsilon_o^2}{1000} \cdot \sum \frac{m_1 Z_1^2}{a_1}$$

so that for comparatively small concentrations we may write as in (10)

$$\log f_1 = \left(\frac{\alpha_A - \alpha_1}{kT}\right)\delta v_1 \cdot \frac{4\pi N\epsilon_o^2}{2D^2.1000} \cdot \sum \frac{m_1 Z_1^2}{a_1} \tag{11}$$

Now if we take a single electrolyte of concentration *m*, each molecule of which yields ν_1 ions of charge Z_1, ν_2 ions of charge Z_2,

$$\sum \frac{m_1 z_1^2}{a_1} = \frac{m_1 z_1^2}{a_1} + \frac{m_2 z_2^2}{a_2} \text{ etc.} = m\left(\frac{\nu_1 z_1^2}{a_1} + \frac{\nu_2 z_2^2}{a_2} + \text{etc.})\right)$$

$$= m\Sigma\nu_1 z_1^2 \left(\sum \frac{\nu_1 z_1^2}{a_1} / \Sigma\nu_1 z_1^2\right)$$

$$= \mu \sum \frac{1}{a_1}$$

where $\mu = m\Sigma\nu_1 z_1^2$ (twice the ionic strength for a binary electrolyte), and $\Sigma\, 1/a$ the mean reciprocal radius of the ions is defined by

$$\sum \frac{\nu_1 z_1^2}{a_1} / \Sigma\nu_1 z_1^2.$$

Thus for a single electrolyte we have

$$\log f_1 = \frac{(\alpha_A - \alpha_1)\delta v_1}{kT} \cdot \frac{4\pi N\epsilon_o^2}{2D^2.1000} \cdot \mu \sum \frac{1}{a_1}$$

and similarly for other ions of kind (2) etc.

$$\log f_2 = \frac{(\alpha_A - \alpha_2)\delta v_2}{kT} \cdot \frac{4\pi N\epsilon_o^2}{2D^2.1000} \cdot \mu \sum \frac{1}{a_1}$$

Thus the mean activity coefficient for the ions of the electrolyte is

$$\log f_{12} = \frac{(\alpha_A - \alpha)\delta v}{kT} \cdot \frac{4\pi N\epsilon_o^2}{2D^2.1000} \cdot \mu \sum \frac{1}{a_1} \tag{12}$$

where $(\alpha_A - \alpha)\,\delta v$ is the mean value of this quantity for all the ions. Now $4\,\pi\,(\alpha_A - \alpha)\,\delta v$ is the mean lowering of the dielectric constant produced by one ion per cubic centimetre, so that

$$D = D_o - 4\pi \frac{(\alpha - \alpha)\,\delta v\,\Sigma m.N}{1000}$$

$$= D_o - \bar{\delta}\,\Sigma\, m.$$

therefore

$$\log f_{1,2} = \bar{\delta}\, \frac{\epsilon_o^2}{2kT\,D^2} \mu \sum \frac{1}{a_1}$$

$$= 4.32 \times 0^{-10}\, \bar{\delta}\, \mu \sum_{i} \frac{1}{a_i} \tag{13}$$

$$\left] \epsilon_0 = 4.77 \times 10^{-10} \text{ e.s. units, } N = 606 \times 10^{23},\ R = kN = 8.31 \times 10^{7} \text{ ergs} \quad T = 293,\ D = 81 \right]$$

The mutual salting out of ions thus gives rise to a term in the expression for log f which is linear with respect to μ. In order to test its importance we may find the values of $\bar{\delta}$ required to produce a coefficient of magnitude B in (5). Thus we have

$$2.303\, B = 4.302 \times 10^{-10}\, \bar{\delta} \sum \frac{1}{a}$$

In the following table the value of *B* (which refer to $\log_{10}$ f, hence the factor 2.303 to convert to natural logarithms) are those given by Harned and Akerlöf,[1] and the values of Σ 1/a are calculated from the ionic radii given by Pauling,[2] except the value for H^+ which is that of W. L. Bragg.[3]

	B	$1/\Sigma\frac{1}{a}$	$\bar{\delta}$(calc.)	$\bar{\delta}$(Hückel)
HCl	0.0805	0.85×10^{-8}	3.65	11.75
LiCl	0.0698	0.90	3.35	10.72
NaCl	0.028	1.24	1.85	6.23
KCl	0.017	1.53	1.39	4.00
$CaCl_2$	0.060	1.17	3.74	11.61
$SrCl_2$	0.030	1.29	2.06	8.93
$BaCl_2$	0.0285	1.48	2.25	7.14

For comparison the last column gives the values of $\bar{\delta}$, required to account for the values of B, according to Hückel's calculation. It is evident that smaller values of $\bar{\delta}$ suffice to account for the linear term regarded as a salting-out effect than those demanded when only the dielectric constant lowering of the medium is taken into account. Both effects probably play their part, and in the absence of reliable data of the dielectric constants of salt solutions and their proper interpretation, we have no means of estimating the magnitude of each. But since quite moderate values of δ appear to be capable of accounting for the observed values of B, estimated as a "salting-out" phenomenon, and since the larger values of Hückel, if extended into concentrated solutions, as the theory demands, would lead to very low or negative dielectric constants in certain cases, it may be that this effect is the more significant.

In this connection it must be remembered that the addition of ions to the solvent does not cause a uniform lowering of the dielectric constant of the medium, but a local "electric saturation" of the molecules in their vicinity.

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[1] Physik. Z., 27, 411 (1926).

[2] J. Am. Chem. Soc., 49, 765 (1927).

[3] Phil. Mag., (6), 40, 169 (1920).

The actual electric forces between the ions will be modified by this to a small extent compared with the effects due to the polarization of the water molecules.

Summary

The effect of the forces exerted by the electric field of an ion on the solvent molecules, on the distribution of other ions in its vicinity, is discussed. A simple derivation of an expression for the salting-out of substances by electrolytes is given and is shown to be equivalent to that obtained by Debye and McAulay on a different basis. The result is applied to the mutual salting-out of ions and it is shown that the effect may be of prime importance in determining B in the equation

$$\log f = -A\sqrt{\mu} + B\mu$$

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CATAPHORESIS OF LEAD SULPHATE

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Colloidal lead sulphate was prepared by mixing two N/200 solutions of lead acetate and sulphuric acid in the cold, using a slight excess of the acid solution. A small portion of this suspension was placed in a covered watch-glass under a microscope and subjected to direct current. The suspended particles moved to the anode showing that the lead sulphate was negatively charged. This is probably due to the adsorption of sulphate ions by the lead sulphate. To check this, another suspension of lead sulphate was prepared adding N/200 H_2SO_4 to a slight excess of N/200 $Pb(NO_3)_2$. The suspended particles moved to the cathode and were therefore positively charged, presumably owing to selective adsorption of lead ions.

When forming a lead peroxide plate in sulphuric acid, the lead sulphate, which is first formed, is held to the lead plate by cataphoresis in addition to a possible adsorption and is therefore in a position to be oxidized to lead peroxide. If we use an alternating current, the lead sulphate which is formed at one moment is carried away by electrical cataphoresis on the reversal and at both electrodes we therefore get lead sulphate which falls to the bottom of the beaker. Under ordinary conditions no appreciable amount of lead peroxide is formed. This shows that under these conditions the adsorption of the lead sulphate by the lead grid is of minor importance in comparison with the cataphoresis effect. This is not necessarily the case. When the spongy lead plate of a storage battery is converted to some extent into lead sulphate on discharge, the lead sulphate is not carried away when the discharged plate is made cathode but is reduced back to spongy lead. When one forms a spongy lead plate by alternate oxidation and reduction, the lead sulphate formed on the oxidation is reduced to lead and not removed when the current is reversed. Slow reversals of the current therefore produce a different result from rapid reversals. We know that a silver chloride precipitate changes on standing so that it becomes more difficult to peptize it with gelatine. We know also that most hydrous oxides change on standing in such a way that it becomes more difficult to peptize them with alkali. We must therefore conclude that lead sulphate on the surface of lead changes with time so that the anode effect of cataphoresis in sulphuric acid solution becomes negligible relatively to other factors.

Since the suspended lead sulphate moved readily to the anode in solutions hours after it had been formed, the important factor seems to be an increased adherence to the lead. It seems probable that there is a time factor in the adsorption and that with time we get an oriented adsorption of the lead sulphate on the lead, which results in the lead sulphate being held more strongly

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* The experiments were done in 1922 as part of the Senior Research under Professor Bancroft. The presentation of the material is of 1929.

by the lead. This does not, of course, exclude the possibility of moderately rapid changes in the lead sulphate taking place when in contact with lead; but there seems to be no reason as yet for making such an assumption.

These experiments throw some light on the Luckow process for the electrolytic preparation of insoluble salts. If one electrolyzes a chromate solution with a lead anode, one first gets a coating of lead chromate on the anode which is then oxidized to lead peroxide just as in the case of a sulphate solution. Luckow uses a mixture of chromate with nitrate or chlorate and gets his lead chromate precipitating away from the anode, so that it is not oxidized farther. The process was tested in the laboratory by Bindschedler and LeBlanc,[1] who got excellent results with a 1.5 percent solution made up 80% of $NaClO_3$ and 20% of K_2CrO_4, in other words an actual concentration of 1.2 percent $NaClO_3$ and 0.3 percent K_2CrO_4. Less satisfactory results were obtained with 1.05 percent $NaClO_4$ and 0.45 percent K_2CrO_4. LeBlanc reports that a preliminary experiment with stirring seemed to indicate that stirring was rather disadvantageous.

LeBlanc's discussion is rather interesting. "If one does the electrolysis in the way prescribed in the patent, the formation of lead chromate actually takes place in a thoroughly satisfactory way. The lead chromate rolls down like an avalanche from the anode, which remains entirely clean, without any formation of a film of lead chromate or lead peroxide. Consequently, the voltage does not increase during the electrolysis. . . .

"What reactions take place in the 'mixed solutions'? How does it happen that addition of sodium chlorate, sodium nitrate, or any similar salt causes a good formation of lead chromate, while there is no formation of an unsatisfactory formation of lead chromate with the same chromate concentration and the same current density but without the other salt being present?

"It seems at first surprising that the presence of completely indifferent ions which take no part in the anode reaction can have such an effect. If we say that the soluble lead salt is first formed, which then reacts with the chromate, that is a meaningless statement. In both cases lead ions are formed at the anode in presence of chromate ions and a reaction of the lead anions with the other anions does not take place at all."

LeBlanc considered the possibility of lead chlorate not being completely dissociated and of that increasing the apparent solubility of lead chromate; but found experimentally that there was no appreciable increase in the solubility of lead chromate on addition of these small amounts of sodium chlorate.

"When sodium chlorate and sodium chromate are both present, both anions move to the anode and the amounts of chromate ions brought to the anode at the same current density are less than if chromate alone were present as anion. The chromate ions react with the lead ions and are removed. Since they are not brought in as rapidly as before, there will be a relative increase in concentration of chlorate ions at the anode and a relative decrease in concentration of chromate ions. If the initial concentration of

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[1] Z. Elektrochemie, 8, 255 (1902).

chromate ions is not too high, *the film in contact with the anode may be freed completely of chromate ions in which case lead ions will form [as lead chlorate], and it will henceforth be impossible for a precipitate to form in immediate contact with the anode.*"

This explanation involves the formation of a practically chromate-free solution of lead chlorate at the anode. Such a state of things would give the results observed and it is evident that stirring would be disadvantageous because it would break up the chlorate film at the anode.

There is another possible explanation, however, If there is formation at the anode of both lead chromate and lead nitrate, the latter only to a slight extent, these lead ions will be adsorbed by the suspended lead chromate, which will be carried away from the anode until the adsorbed lead ions react with chromate ions in the solution. This would tend to form a practically chromate-free film at the anode just as in the other case; but with this difference, that the chromate-free film is not essential if we are dealing with cataphoresis. On the colloid-chemical explanation, stirring would be advantageous, because it would help the cataphoresis process to remove the lead chromate from the neighborhood of the anode. On the LeBlanc explanation stirring is disadvantageous, because it destroys the practically chromate-free film at the anode. It should therefore be easy to determine which of the two explanations is the better.

Two percent solutions by weight of sulphuric acid and of nitric acid were made up and were mixed in varying proportions. This rather crude way of doing things was adopted because both Luckow and LeBlanc used weight units and not gram-equivalents or gram-molecules. A cylindrical, rotating, lead anode was placed between two lead cathodes and the anode current density was made 0.005 amp/cm^2 as was done by LeBlanc and Bindschedler. In all cases the stirring was found to be beneficial. The Luckow process seems therefore to be one involving cataphoresis.

Cataphoresis plays a part in the electrolytic determination of lead. There is no way that lead ions can be carried to the anode and there is no reason at present to assume the existence of any appreciable amount of lead as part of a complex anion. Consequently the only lead ions that can be oxidized to plumbic lead are those which happen to be at any moment in contact with the anode. This part of the thing is similar to the electrolytic oxidation of alcohol, which is assumed not to be transferred in either direction by the current. It seems that the current efficiency in the oxidation of lead would be increased markedly by stirring the solution. Since that is done normally in most electrolytic analyses nowadays, the theoretical significance of it might easily have been overlooked. After the plumbic ions have been oxidized, cataphoresis carries the negatively-charged lead peroxide[1] against the anode.

Cornell University,
June, 1922.

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[1] Weiser: "The Hydrous Oxides," 231 (1926).

ISOMERISM AND CONFIGURATION*

BY A. C. LUNN AND J. K. SENIOR

I. Introduction

Foreword.—The general ideas of isomerism and the configuration of molecules have been treated by so many different investigators and from so many different points of view that limitations of space practically forbid any attempt at a connected review of these subjects. In the present paper, therefore, historical aspects will be mentioned only in so far as the articles cited bear directly on the theory and formulae herein developed. Another form of introduction, however, appears to be unavoidable. Since the discussion is to be largely mathematical, it is necessary to review certain current chemical terms and to define with adequate precision the sense in which these will be used. At the same time, there will be introduced certain new expressions which in part refer to new ideas, and in part consist only of names applied to old but hitherto unnamed concepts.

Pure Substances.—The terms "atom," "molecule" and "valence" are here accepted in the sense in which they are ordinarily used. For the moment at least they require no more precise definition. "Isomerism" however is a relation existing between "pure substances" which are not objects of experiment but ideal limits to series of separation processes. And just what is meant by a pure substance is by no means free from ambiguity.

To begin with, it is not assumed that all the molecules of a pure substance are in an identical condition. Modern theories of chemical reaction usually assume that in any lot of material certain molecules exist in an "activated state," and that the activated molecules are in dynamic equilibrium with the unactivated ones. But it is never assumed merely because some of the molecules are activated while others are not that the substance is therefore a mixture—or in other words impure. On the other hand, aceto-acetic ester is generally agreed to be a "tautomeric" mixture of two isomeric substances, the enol and the keto forms, which are in dynamic equilibrium with one another. The separation of these two forms is difficult but not impossible.

Between such tautomeric mixtures at one extreme and the so-called pure substances containing activated molecules at the other, there may or may not exist an unbroken series of intermediate cases. It is certain that there are some tautomeric mixtures which are more difficult to separate into their component pure substances than is aceto-acetic ester. In some of these cases a partial but not a complete separation has been accomplished. Easily racemized pairs of optical isomers fall in this class. Certain other materials in which no separation has ever been effected nevertheless resemble tauto-

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* Contribution from the Kent Chemical Laboratory and the Department of Mathematics of the University of Chicago.

meric mixtures so closely that it seems justifiable to assume that they also consist of two or more isomeric forms in dynamic equilibrium.

By contrast, the current theory[1] in regard to hexahydro-benzene is that this substance consists of at least two different forms also in dynamic equilibrium. With the methods at present available, however, there seems to be almost no chance of separating these components. Again, the Kekulé formula for benzene calls for two forms of all ortho-disubstituted benzene derivatives, and here also the members of the various pairs are supposed to be in dynamic equilibrium. No one has ever met with any success in attempts to isolate the members of such a pair. Further, the rotation dispersion phenomena in tartaric acid and some of its derivatives have given rise to the hypothesis that in the fluid states these substances are equilibrium mixtures of several distinct forms.[2] And lastly, the question of whether solutions of certain pentaerythrite derivatives contain only one variety of these substances, or whether some of the molecules may be in a tetrahedral and others in a pyramidal form has been argued at some length.[3] There appears to be no record that any attempt has been made in the last two cases to isolate the individual forms supposed to constitute the mixture, but the present prospects of such an isolation are to say the least discouraging.

A successful mathematical theory of isomerism should certainly permit the number of isomers in a given class to be calculated, and it seems futile to attempt to devise such a theory if the activated and unactivated molecules in a pure substance be considered isomeric. For it is never certain just how many varieties of activated molecules exist in a sample of such material, and so there is no means of comparing the numerical consequences of any theory with observed facts. Similarly, as long as the object of enumeration is kept in mind, supposed varieties like those of hexahydro-benzene, ortho-disubstituted benzene derivatives, tartaric acid or pentaerythrite can hardly be considered as isomers. Present knowledge of these variations in molecular structure and configuration is too small to permit of an accurate counting of the varieties in the so-called equilibrium mixtures.

In other words, the authors of this paper do not consider it at present advisable to treat the cases intermediate between tautomerism and activation as forming a smooth and unbroken series. The criterion of separability (partial or complete) serves to divide this series with the requisite degree of distinctness, provided it is used under the guidance of practical judgment in a somewhat extended sense. Certain cases where no actual separation has yet been made may be treated as separable on the grounds of analogy with cases where

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[1] Sachse: Z. physik. Chem., 10, 203 (1892); Ber., 23, 1363 (1890); Mohr: J. prakt. Chem. (2), 98, 315 (1918).

[2] Arndtsen: Ann. Chim. Phys., (3) 54, 403 (1858); Lowry: J. Chim. phys., 23, 565 (1926); Longchambon: Compt. rend., 178, 951 (1924); 183, 958 (1926); Lucas: Ann. Phys., (10) 9, 381, (1928).

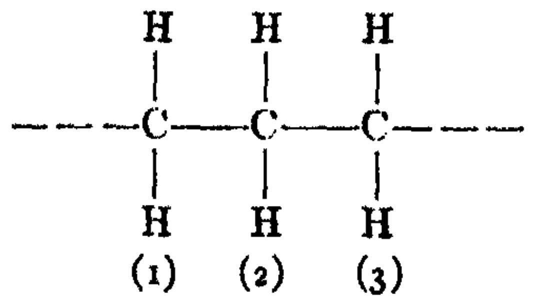
[3] Ebert and v. Hartel: Naturwissenschaften, 15, 669; Weissenberg: 662 (1927); Boeseken and Felix: Ber., 61, 787, 1855; Kenner: 2470 (1928); Ebert, Eisenschitz and v. Hartel: Z. physik. Chem., [B] 1, 94 (1928).

such a separation is an experimental fact. A criterion which is strictly free from ambiguity in all instances seems at present unattainable.

Of course a distinction based on separability assumes the present state of chemical technique. It is probable that substances inseparable today may, in view of improvements in chemical methods, be separated to-morrow. But this prospect of improvement is not subject to any known limitation, and consequently to postpone all attempts at a mathematical theory of isomerism until the perfection of available methods of separation would be equivalent to the abandonment of such attempts. Nor does there seem to be any reason why the present status of chemistry should be considered particularly ill-suited to supply the foundation of such a theory. On the contrary, there is some reason to believe that it may be particularly well adapted to serve this purpose.

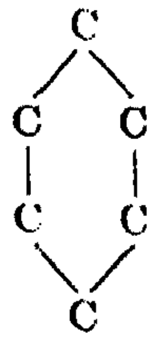
Connexity and Configuration.—From the percentage elementary composition and molecular weight of any pure substance, its empirical formula is calculated. With such empirical formulae in hand, it has been possible to work out the connexity relations between the component atoms of the molecules of a large number of substances. These connexities are arrived at principally by interpretation of the synthetic, disruptive, and replacement reactions which form the bulk of structural chemistry. The present paper need not attempt to deal with this side of the subject; the connexity data are assumed in their ordinarily accepted form.

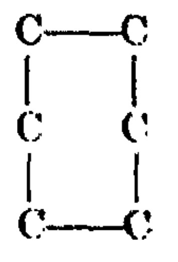
It is important however to note that connexity data do not by themselves determine the space relations of the atoms in the molecule. Saturated unbranched hydrocarbon chains are usually written in something like the following form:

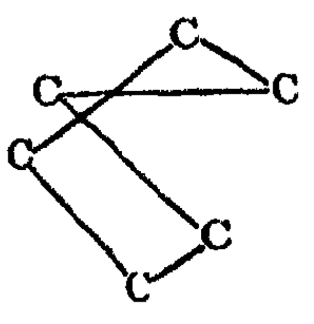


$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ --- & C & — & C & — & C & --- \\ & | & & | & & | & \\ & H & & H & & H & \\ & (1) & & (2) & & (3) & \end{array}$$

But this conventional mode of representation is not supposed to indicate that the hydrogen atoms directly connected with carbon atom (2) really lie closer to this atom than they do to carbon atom (3), or that carbon atoms (1) and (2) really lie closer to one another than do carbon atoms (1) and (3). Similarly, the simple statement that the six carbon atoms in benzene are cyclically connected is compatible with a great number of diagrams of which the following may be considered samples.







The attempt to rule out from such a list of possibilities all but one form (or failing that a minimum number of forms) is the attempt to establish the configuration of the molecule, and all data which aid in this process of elimination are "configuration data" as distinguished from the "connexity data" hitherto referred to. It is of course possible that in a particular case a single observed fact may be part of both bodies of data. And it is obvious that while the connexity[4] data can always be adequately represented in two dimensions, the configuration data usually need three.

Skeleton and Univalent Substituents.—If the structural (connexity) formula of a compound be written out in full, it will be seen that the molecule can be thought of as a skeleton carrying a certain number of univalent substituents. The skeleton may be a single atom, a straight or branched chain, a single or condensed ring, or any complex of such forms. Since radicals as well as atoms may be treated as univalent substituents, the division of the molecule is not unique. For example, in xylene, at least three methods of division at once suggest themselves.

(1) The skeleton consists of the eight carbon atoms of the xylene molecule; the univalent substituents are the ten hydrogen atoms attached to this skeleton.

(2) The skeleton consists of the six carbon atoms of the benzene ring; the univalent substituents are the two methyl groups and the four hydrogen atoms attached to this skeleton.

(3) The skeleton consists of the six carbon atoms of the benzene ring and the two methyl groups; the univalent substituents are the four hydrogen atoms attached to this skeleton.

Any one of these methods of division is admissible. The choice between them depends on the object in view.

But although the choice of a skeleton may in some cases be somewhat arbitrary, each possible choice fixes a certain resultant set of properties of the system. In the first place, the number d of univalent substituents (always a positive integer) is thereby uniquely determined.[5] In the second place, choosing a skeleton in such a way that a particular atom or radical (A) functions as a univalent substituent is equivalent to assuming (at least for the purposes of the present discussion) that (A) has certain properties. From the moment that (A) is so chosen, it is to be considered as an indivisible unit, and as such it acquires the infinite symmetry usually represented by a geometrical point, and becomes permutable with other univalent substituents supposed to possess like properties. That is to say, when such univalent atoms or radicals

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[4] Connexity is a relation of order independent *of considerations of space.* The "structural" relations treated by chemists are relations of just this sort, and it is unfortunate that the word structure as used by engineers, etc., should carry with it geometrical connotations which are too special for chemistry. Throughout the present article "connexity" and "structure" are used as synonyms, and the former expression is introduced here merely to emphasize the fact that the relations indicated by both terms are independent of space limitations, except perhaps the vague one implied in the word vicinity.

[5] Molecules like CO_2 and N_2 which *do not contain* any univalent atom or radical may be considered as cases where $d = 0$. Such molecules do not give rise to instances of isomerism of the kind treated in this paper.

as hydrogen, iodine, methyl or naphthyl are thought of as univalent substituents, the differences between them become qualitative, like the differences between red, blue, and yellow geometrical points. From these considerations arises a certain limitation on the choice of univalent substituents which will be discussed later in connection with enantiomorphism.

Partitions.—It is next necessary to define certain purely mathematical terms which at this point assume an essential role in the discussion. If d and $d_1, d_2 \ldots . d_f$ are positive integers such that $d_1 + d_2 \ldots . + d_f = d$, then the set of integers $d_1, d_2 \ldots . d_f$ is called a partition of d, and each such set may be designated as a value of the general symbol (p). Every value of (p) naturally determines the corresponding value of d; and d determines a finite set of values for (p). The number of values of (p) in such a set is q(d)— a single-valued, positive, integral function of d.

If d is considered constant, there will be distinguishable among the values of (p) certain pairs which may be called adjacent. When the transfer of a single individual from one class to another converts (p_a) into (p_b), then these two partitions are adjacent. For example, where d is 6, the partition (4, 2) is adjacent to the partitions (5, 1), (4, 1, 1), (3, 3) and (3, 2, 1). It is not adjacent to the partitions (2, 2, 2), (3, 1, 1, 1), etc.

When any molecule is divided into a skeleton and univalent substituents, not only is the number d of univalent substituents thereby fixed, but a value for (p) is also determined, since the univalent substituents chosen must consist of a certain number of classes of like individuals.

Type Properties and Specific Properties.—With these ideas in mind, the properties of molecules may be divided into two kinds as follows.

I. Type properties are determined by the nature of the molecular skeleton, the value of (p) and the distribution of the various sorts of univalent substituents among the unsatisfied valences of the skeleton.

II. Specific properties are not completely determined by the considerations just mentioned, but depend also on the specific nature of the atoms or radicals which function as univalent substituents.

An example will make this general statement somewhat clearer. Suppose that the skeleton be the carbon ring of benzene so that d is 6. In hydroquinone, the value of (p) is (4, 2). Now it is a property of hydroquinone that if one of the hydrogen atoms which function as univalent substituents be replaced by some univalent substituent other than a hydrogen atom or a hydroxyl radical (whereby a substance is produced for which (p) is (3, 2, 1)), the compound formed is the same whichever hydrogen atom is replaced. This property of hydroquinone is however a type property. It is dependent only on the nature of the benzene carbon skeleton, the adjacent partitions (4, 2) and (3, 2, 1), and the distribution of the various univalent substituents in the original compound into the para position. Statements perfectly analogous to the one just made for hydroquinone could be made about para-dinitrobenzene, para-dimethyl-tetrachloro-benzene, etc. On the other hand, hydroquinone is a powerful reducing agent. This, however, is a specific property dependent on the fact that the para pair of like univalent substituents which form one class are hydroxyl groups. No similar reducing property is found in para-dinitro-benzene, para-dimethyl-tetrachloro-benzene, etc.

From what has been said, it is clearly of importance to have a complete list of the type properties of molecules. For it may be stated at once that, although a general theory of isomerism competent to explain type properties seems well within reach, a theory which accounts for specific properties is still some distance in the future. Further discussion of these type and specific properties is however postponed until the subject of isomerism has been considered in greater detail.

Isomerism and its Varieties.—For treating this subject, the following definitions will be used.

(1) If any experimental procedure serves to distinguish under like conditions between two lots of pure material of identical empirical formula, then these two lots of material are specimens respectively of two isomeric compounds. Isomerism is the relation existing between them. The use of connexity data makes possible the extension of this idea to include the idea of isomeric radicals.[6]

(2) Structural isomers are isomeric substances which differ in regard to the connexity relations within their respective molecules; stereo-isomers show no such difference.

(3) Physical isomers are substances which as solids show different properties but which are alike in the fluid (that is the gaseous, liquid or dissolved) states.

(4) Diamers are best defined indirectly; diamerism is the relation between any two stereo-isomers which are not enantiomorphs. (See Note A.)

Enantiomorphism.—(5) Enantiomorphism or optical isomerism is a special form of stereo-isomerism. If two substances (A) and (B) show the following properties, they are called enantiomorphs or optical isomers.

(a) (A) and (B) in the fluid states rotate the plane of polarized light equally but in opposite directions. That is, they are both "optically active," *and the optical activity of (A) is the negative of that of (B).* In the crystalline state, certain special effects obtained from (A) are equal to those obtained from (B), but of opposite sign; of these the piezo-electric phenomenon is the best known. Usually (but not invariably) the crystals of (A) are not congruent with the crystals of (B), but are congruent with the mirror images of such crystals.

(b) (A) and (B) are identical in respect to all ordinary physical properties, and identical in their chemical behavior towards all reagents except those

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[6] Throughout the present paper, it will be necessary to refer repeatedly to the number N of isomers in a given class. The equation $N = 1$ is therefore equivalent to the assertion that the number of isomers is one. In spite of the somewhat paradoxical nature of this language, such use of the terminology is indicated by considerations of brevity and uniformity. And so hereafter, when the number of isomers in a given class is said to be one, the statement should be understood to mean that there is only one compound in the class in question. This implies that there is no isomerism at all. Interpreted in this fashion, the terminology has never been found to lead to confusion.

which are themselves optically active in the fluid states. It is understood to be typical that they differ in their chemical behavior towards optically active reagents, although the amount of difference may in some cases be too small to measure.

Such is the ordinary definition of enantiomorphism. The usual interpretation is that enantiomorphous molecules possess space configurations which are non-congruent mirror images of one another. But it is possible to define enantiomorphism with equal accuracy and in more abstract terms as follows.

Let S be a complete class of isomers containing every substance or every radical of given empirical formula. The enantiomorphous relation E is such that

I Every class S is uniquely divided into two subclasses S′ and S″ such that
  (a) For every member u of S′ there exists a member v of S such that u E v.[7]
  (b) For every member x of S″ there exists no member y of S such that x E y.

II (a) u E v implies that u and v are not identical.
  (b) u E v implies v E u.
  (c) u E v and u E v′ imply that v and v′ are identical.

That is to say, enantiomorphism is the only symmetric, intransitive and constantly dyadic relation found among the isomers of a complete class S.

At this point it is probably best to introduce parenthetically the limitation on the choice of univalent substituents already referred to (see p. 1031). It is as follows: Every univalent substituent x must be such that there nowhere exists a univalent substituent y such that x E y. Because if x E y, then x cannot be considered to possess the infinite symmetry representable by a geometrical point, and cannot therefore be permuted with the univalent substitutents considered to possess such symmetry.

Skeletal Isomerism and Univalent Substitution Isomerism.—(6) The various categories of isomers so far mentioned are well recognized by chemists and their names are firmly established in the literature. But there is another easily definable kind of isomerism for which no special name is current. The division of any molecule into skeleton and univalent substituents implies a unique division into two classes of the isomeric relations between compounds of the empirical formula in question.

I. Univalent substitution isomerism is the relation existing between compound (A) and the isomeric compound (B) if the formula of (A) can be converted into that of (B) by a permutation of the univalent substituents without disturbing the skeleton. In this case (A) and (B) are univalent substitution isomers.

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[7] The notation u E v is a customary one to denote that u stands in the relation E to v.

II. Skeletal isomerism is the relation existing between compound (A) and the isomeric compound (B) if the formula of (A) cannot be converted into that of (B) without disturbing the skeleton. In this case (A) and (B) are skeletal isomers.

Although the terms just defined are new, there is nothing novel in the ideas involved. Hence many examples of these two kinds of isomerism will occur to any trained chemist, and two pairs of typical examples will suffice at this point.

(1) If the skeleton is the three-carbon-atom chain of propane, normal propyl chloride and iso-propyl chloride are univalent substitution isomers.

(2) Toluidine and picoline are skeletal isomers.

It seems probable that this distinction is essential for any practicable mathematical theory of isomerism.

Classification and Enumeration of Isomers.—When all the forms of isomerism hitherto defined[3] are taken into account, it may be seen that there exists within a complete class of isomers a complicated system of interlocking subclasses. In certain cases the same term has been used to apply to relations of quite different sorts. For example, if, in lactic acid, the so-called "asymmetric carbon atom" be chosen as a skeleton, and the methyl, hydroxyl and carboxyl radicals and the hydrogen atom be the four univalent substituents, then the enantiomorphism existing between dextro and laevo lactic acids is an instance of univalent substitution isomerism. The enantiomorphism between dextro and laevo camphor is an instance of skeletal isomerism. The two borneols (dextro and laevo) are enantiomorphs and skeletal isomers; dextro borneol and dextro isoborneol are diamers and univalent substitution isomers; dextro borneol and laevo isoborneol are diamers and skeletal isomers. The members of all three pairs are stereo-isomers. And examples of various other combinations of different sorts of isomerism may be found.

The categories defined give a fair idea of the experimental distinctions recognized by present-day chemistry. It should not be imagined, however, that the scheme here presented possesses any sort of exclusive validity. At any time some generalization broader than any now current may classify together substances between which there is now no recognized connection, and relegate the whole problem of isomerism to the status of a phase of some larger problem not now distinctly admitted as such. At any time a method of separation finer than any now known may divide what now appears to be a single substance into a class of isomers. At any time a new experimental method may group the members of a class of isomers into a set of subclasses, thus introducing a stage of classification intermediate between any two stages now explicitly recognized.

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[3] The list takes no account of the varieties of isomerism known as "tautomerism" and "epimerism." These terms are based on dynamic considerations, and indicate a tendency on the part of the substances in question to be converted into one another with more than usual ease. Since the degree of ease of this conversion is a relative matter, the terms in question do not lend themselves to precise definition. For this reason and because they refer to highly specific properties, no account will be taken of them in the present article.

But although the scheme of classification outlined may be amplified in a variety of ways, it is hardly possible that any of it can be destroyed. The number of isomers is essentially the number of members of a class. And what this number may be is a meaningless question until the class to be enumerated has been defined. The choice of such a definition is almost completely arbitrary. It is only necessary that the definition chosen be self-consistent. If it fulfills this one requirement, and if, once chosen, it be adhered to unchanged throughout the subsequent enumeration, the results (assuming the experimental data to be right) may perhaps be uninteresting or unfruitful, but cannot rationally be called incorrect.

To define a class of isomers for enumeration is to agree in advance just what varieties of isomerism shall be recognized during that enumeration. And although all such defining agreements (provided they are self-consistent) are logically on a par with one another, it is an historical fact that certain particular defining agreements have proved themselves very useful and played important roles in the history of chemistry, while others have never led to results of much interest and have consequently attracted but little attention. The difference between those defining agreements which have been of importance and those which have not is intimately connected with the matter of the type and specific properties of molecules. Hence these two subjects will be discussed together, the object being to indicate just which defining agreements recognize some or all of the differences in the type properties of molecules without taking account of any differences in their specific properties.

The Fluid States.—To begin with the subject of physical isomerism, it is well known that the property possessed by some pure liquids of crystallizing in physically isomeric forms is highly specific. For example, the fact that benzophenone possesses this property does not indicate that either acetone or dekachloro-benzophenone acts in a like manner. Throughout the remainder of this paper, physical isomerism will receive no further recognition, and attention will be confined to such isomers as have an independent existence in the fluid states.

Along with this restriction of attention to the fluid states, goes an important limitation on the use of the word "molecule," and the division of any molecule into a skeleton and univalent substituents. A molecule throughout the ensuing argument is thought of as a cluster of atoms united by a valence structure. Whether or not such a cluster carries an electric charge is beside the point. Consequently no account is here taken of those substances which in the fluid state show the phenomenon of electrolytic dissociation, since it is generally agreed that there is no structural connection between the ionic products of such a dissociation.[9] But if one of these products is a complex ion, then this ion by itself may be treated in just the same way as an uncharged molecule. That is to say, the division of the ammonium chloride molecule into a skeleton (consisting of the nitrogen atom) and five univalent substituents is barred from consideration. On the other hand, the division of the

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[9] See e.g. Sidgwick: "The Electronic Theory of Valency," p. 84, (1927).

ammonium ion into a skeleton (consisting of the nitrogen atom) and four univalent substituents, disregarding entirely the existence of the chloride ion, is fully contemplated in the present work. In other words, throughout the remainder of this paper, the word "molecule" shall be understood to stand for the phrase "molecule or complex ion," and the particular significance appropriate to the case in hand is to be attached to it.

The Number of Univalent Substitution Isomers.—If any molecule be divided into a skeleton V and d univalent substituents, the number $N_V(p)$ of univalent substitution isomers which may be formed by attaching these d substituents to the skeleton in all possible ways is obviously a function only of the nature of the skeleton and the value of (p). That is to say, the number $N_V(p)$ is a type property independent of the specific nature of the univalent substituents. This general assertion merely puts into words an idea so fundamental for organic chemistry that it is usually implicitly assumed rather than explicitly stated. It probably seldom occurs to any organic chemist to inquire whether the existence of only one methyl chloride implies that there is only one methyl alcohol, one iodoform, one triphenylmethane, etc., and, if so, why; or whether the existence of three tribromo-benzenes implies that there are just three benzene-tricarboxylic acids, three trichloro-trinitro-benzenes, etc., and, if so, why this should be the case. But if implications such as these were not justified, structural and stereo-chemistry could hardly exist in anything like their present form. Whatever success these branches of chemistry have had in arranging and codifying the data is evidence for the correctness of the idea that the number $N_V(p)$ of univalent substitution isomers belonging to a given skeleton V and a given partition (p) is a type property.

The statement just made, however, is to be taken with an important reservation concerning the choice of the skeleton when particular kinds of univalent substituents are contemplated, namely that if the skeleton contains any univalent atom or radical (A), then no similarly connected univalent substituent is to be identical with (A). An example will illustrate the reason for this reservation. Suppose that the skeleton chosen be the two carbon atoms and single chlorine atom of ethyl chloride. Then d is 5. Let (p) be (4, 1), and consider the special case of four hydrogen atoms and one bromine atom. The number of univalent substitution isomers is 3. This number 3 is independent of the specific nature of the univalent substituents as long as no one of them is a chlorine atom. But if the five univalent substituents consist of one chlorine atom and four hydrogen atoms, the number of isomers is two; and if the univalent substituents consist of four chlorine atoms and one hydrogen atom, the number of isomers is one. Thus, without the restriction mentioned, the number of univalent substitution isomers ceases to be a type property and becomes in part at least specific. Hence, in all that follows, it will be assumed that the molecule has been divided into a skeleton and univalent substituents in such a way as to comply with the above limitation.

This does not mean that the number of monochloro- or tetrachloro-derivatives of ethyl chloride cannot be determined. The numbers of these derivatives are the same as the numbers of the dichloro- and pentachloro-derivatives of ethane. To determine these numbers, the skeleton is chosen so that d is 6, and the number of dichloro- and pentachloro-derivatives is obtained by letting (p) be (4, 2) and (5, 1) respectively in the two cases.

Where the skeleton contains no univalent atoms or radicals, there is no similar restriction on the choice of univalent substituents.

The Number of Enantiomorphous Pairs.—If the skeleton V is a single carbon atom, and (p) is (1, 1, 1, 1), then $N_V(p)$ is 2. This number 2 has already been shown to be a type property. But it may further be stated in this case the two isomers are enantiomorphs, and one of the essential features of the van't Hoff doctrine of the "asymmetric carbon atom" is that the enantiomorphous relation between the two isomers in question is a type property. That is to say, when V is a single carbon atom and (p) is (1, 1, 1, 1), the two isomers must be enantiomorphous, irrespective of the specific nature of the univalent substituents involved. And the wide success of the van't Hoff theory is confirmation of the correctness of this idea. (See Note B).

When the skeleton is more complex than a single carbon atom, enantiomorphism still continues to be a type property. If the skeleton is the three carbon atom ring of cyclopropane, and (p) is (4, 2), then $N_V(p)$ is 4. Two of these four isomers form an enantiomorphous pair while the other two do not, irrespective of the specific nature of the univalent substituents. Again, where V is the six carbon atom ring of hexahydro-benzene, and (p) is (10, 2), then $N_V(p)$ is 9; and of these nine isomers exactly four always occur as two enantiomorphous pairs.

The Number of Structurally Isomeric Subsets of Univalent Substitution Isomers.—In some sets of univalent substitution isomers certain subsets may be recognized. The members of each such subset are stereo-isomerically related. The relation between members of different subsets is one of structural isomerism. For example, if V is two carbon atoms joined by a single bond, and (p) is (2, 2, 2), then $N_V(p)$ is 6. The number of subsets as defined above is 4. One of them contains three isomers, the other three contain one compound each. And exactly the same relations hold whether the substances in question be isomers of tartaric acid, of dimethyl-succinic acid or of diphenylglycol. It should be clear without further argument that the number of such subsets and the number of isomers in each subset are in all cases type properties.

Certain Classes of Isomers based on Type Properties.—To sum up, if $S_V(p)$ is a set of univalent substitution isomers determined by a given skeleton V and a given value of (p), then the number of members of $S_V(p)$, the number of enantiomorphous pairs in $S_V(p)$ and the number of subsets of $S_V(p)$ between which there exists a structurally isomeric relation are all type properties. Hence the following three defining agreements in regard to classes of isomers to be enumerated involve only type properties.

(1) The univalent substitution isomers derived from one skeleton, taking account of isomerism, structural and steric, both enantiomorphous and diameric. The number in the class $S_V(p)$ so defined is $N_V(p)$.

(2) The univalent substitution isomers derived from one skeleton, taking account of structural isomerism and diamerism, but disregarding enantiomorphism by counting each enantiomorphous pair as one individual. The number in the class $S'_V(p)$ so defined is $N'_V(p)$.

(3) The univalent substitution isomers derived from one skeleton, taking account only of structural isomerism, and disregarding stereo-isomerism by counting each subset of stereo-isomers as one individual. The number is the class $S''_V(p)$ so defined is $N''_V(p)$.

If V and (p) are constant, then $N_V(p) - N'_V(p)$ is the number of enantiomorphous pairs in $S_V(p)$.

Complete Sets of Isomer Numbers.—If all the q(d) values of (p) determined by a single value of d are considered in connection with any given skeleton V, there are obtained sets of q(d) numbers which may be called respectively complete sets of $N_V(p)$s, $N'_V(p)$s or $N''_V(p)$s. In any such set there is always the peculiar case that $N_V(p)$, $N'_V(p)$ and $N''_V(p)$ are all equal to one when (p) = (d), no matter what V may be. That is to say, if the unsatisfied valences of any skeleton V are saturated by d identical univalent substituents, only one compound can be formed. There are therefore just as many types of compound determined by V and (p) = (d) as there are determined by V alone.

Skeletal Isomerism.—If the class of isomers to be enumerated is to contain skeletal isomers, then the results at present most interesting are obtained by imposing a further restriction on the method of dividing the molecule into a skeleton and univalent substituents. This is to be done in such a way that

(1) No univalent substituent is a polyatomic radical.

(2) No univalent atom is part of the skeleton.

If the division is performed in this unique manner, then the problem of finding the total number of isomers of given empirical formula resolves itself into two separate problems as follows:

(a) The problem of finding in how many ways the skeletal atoms can be connected in a single skeleton V with d unsaturated valences. The class of all such skeletons is T; the number of members of T is N_T.

(b) The problem of finding the number of univalent substitution isomers derivable from each member of T.

Although these two problems are so closely related chemically that the distinction between them seems almost artificial, from the point of view of the mathematical methods required, they show important differences. Problem (b) (which has already been discussed in some detail) is directly a problem in partitions and permutation groups;[10] problem (a) involves also preliminary consideration of a method of representing connexity between polyvalent atoms. Of the two, (a) is thus distinctly the more complex.

The value of N_T is a function only of the nature of the skeletal atoms and the value of d. It is independent not only of the specific nature of the univalent substituents but also of (p). But since the value of N_T is a type pro-

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[10] The word "substitution" is used by chemists and mathematicians in conflicting senses. Throughout the present article this word is to be understood to have its ordinary chemical significance; for the mathematical term "substitution" the expression used is "permutation"—a usage for which there is good mathematical precedent.

perty and the number $N_V(p)$ of univalent substitution isomers derivable from each member of T is likewise a type property, the total number of isomers of given empirical formula is also a type property. From this and similar reasoning, it is clear that the following three additional defining agreements as to classes of isomers to be enumerated also involve only type properties.

(4) The isomers of given empirical formula, taking account of isomerism, structural and steric, both enantiomorphous and diameric. The number in the class U(p) so defined is Q(p).

(5) The isomers of given empirical formula, taking account of structural isomerism and diamerism, but disregarding enantiomorphism by counting each enantiomorphous pair as one individual. The number in the class U′(p) so defined is Q′(p).

(6) The isomers of given empirical formula, taking account only of structural isomerism and disregarding stereo-isomerism by counting each subset of stereo-isomers as one individual. The number in the class U″(p) so defined is Q″(p).

On account of the disparity in the mathematical machinery necessary for the solution of problems (a) and (b) (p. 1038) it seems unlikely that the values of Q(p), Q′(p) and Q″(p) can be conveniently given by any single formula. It is easy to show that $N_V(p)$, $N'_V(p)$ and $N''_V(p)$ can be represented as the sums of series, and hence Q(p), Q′(p) and Q″(p) as the sums of series each member of which is itself a series. In certain cases, however, a simple expression exists. If (p) = (d), then only one type of univalent substitution derivative may be formed from each member of T. Hence the number of isomers of given empirical formula is N_T. In this case, (b) is vacuous and (a) is the whole problem. On the other hand, where the skeleton consists of less than three atoms, the value of N_T is usually one,[11] and

$$\begin{aligned} Q(p) &= N_V(p) \\ Q'(p) &= N'_V(p) \\ Q''(p) &= N''_V(p) \end{aligned}$$

Here (a) is vacuous and the whole problem lies in (b).

In the literature there are a number of attempts to deal with the matter of skeletal isomerism. The two papers of widest scope are those of Sylvester[12] and of Gordan and Alexejeff,[13] in both of which the parallelism between the chemical theory of molecular structure and the algebraic theory of invarients is stressed. It seems probable that interesting and important results might be attained by exhaustively pursuing this line of attack, but chemists have never devoted to these papers the attention which they deserve.

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[11] The case where V consists of one carbon and one nitrogen atom and d is one is an exception to this rule.

[12] Sylvester: Am. Jour. Math., 1, 64 (1878). See also Clifford: ibid., p. 126.

[13] Gordan and Alexejeff: Z. physik. Chem., 35, 610 (1900).

Cayley[14] set himself a more restricted problem by considering only open chain skeletons composed entirely of one kind of atom. His work attracted considerable notice and called forth a number of articles purporting to contain improvements on his methods.[15] But the formulae for the numbers of isomers developed in these papers, although in many cases correct, are never convenient to apply, and some of them involve so large an amount of enumeration and summation that they represent only a moderate advance over the graphic methods which they are intended to replace. It it is further noteworthy that all of these articles (Cayley's included) are restricted to the field of structural isomerism, and that even within this limited range the various authors do not always agree on the isomer numbers obtained. The intricate nature of the problem is thus clearly indicated.

Since the systematic treatment of problem (b) appears to be a natural first stage in the treatment of the more general questions raised by problem (a), this article deals no further with skeletal isomerism. It is hoped to take up this subject at some future time, when the papers cited will be further discussed.[16] For the present, attention will be confined to the study of the classes $S_V(p)$, $S'_V(p)$ and $S''_V(p)$ as well as the determination of $N_V(p)$, $N'_V(p)$ and $N''_V(p)$ which enumerate these classes.

Genetic Relations.—But before the details of these problems are considered, attention may be called to another type property which has been familiar to chemists at least since 1875, but to which no special name has apparently been applied. Let $S_V(p_a)$ and $S_V(p_b)$ be two sets of univalent substitution isomers determined by V and the adjacent partitions (p_a) and (p_b). Since the partitions are adjacent, the two sets of isomers may be called adjacent sets. In favorable cases, each member of $S_V(p_a)$ may be converted by simple subsitution reactions into one or more members of $S_V(p_b)$. That is to say, each member of $S_V(p_a)$ is genetically connected with a certain number of members of $S_V(p_b)$, and the number of members of $S_V(p_b)$ genetically connected with each member of $S_V(p_a)$ is a type property. If the genetic relations of all members of $S_V(p_a)$ with all the members of $S_V(p_b)$ be considered together, then they may be called the genetic relations of $S_V(p_a)$ and $S_V(p_b)$, and these relations are also type properties.

A classic example of the use of these genetic relations is found in Körner's work on the substitution derivatives of benzene. Körner took the carbon ring of benzene as a skeleton V, and investigated the adjacent sets of isomers $S_V(4, 2)$ and $S_V(3, 3)$. $N_V(4, 2)$ and $N_V(3, 3)$ are both 3. He found that a certain member (A) of $S_V(4, 2)$ is genetically connected with only one member (D) of $S_V(3, 3)$; a second member (B) of $S_V(4, 2)$ is genetically connected with

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[14] Cayley: Brit. Ass. Adv. Sci., Reports, p. 257 (1875); Phil. Mag., (4) **47**, 444 (1874); (5), **3**, 34 (1877). These papers are reprinted in Vol. IX of Cayley's collected works.

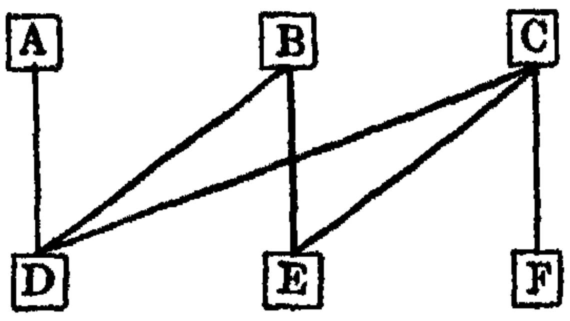
[15] Schiff: *Ber.*, **8**, 1542 (1875); Losanitsch: *Ber.*, **30**, 1917; Herrmann: 2423 (1897); Delannoy: Bull., (3), **11**, 239 (1894).

[16] A general method of determining in terms of the group theory the number of isomers of arbitrary empirical formula has already been obtained.

two members (D and E) of $S_V(3, 3)$; and the third member (C) of $S_V(4, 2)$ is genetically connected with all three members (D, E and F) of $S_V(3, 3)$. These relations are illustrated schematically by the following diagram.

(p) = (4,2) N (4,2) = 3.

(p) = (3,3) N (3,3) = 3.



They are sufficient to identify each one of the six substances involved and serve as the basis for assigning names as follows. (A) is the para, (B) the ortho and (C) the meta isomer in $S_V(4, 2)$; (D) is the asymmetric, (E) the vicinal and (F) the symmetric isomer in $S_V(3, 3)$.

Körner actually carried out this investigation on the dibromo- and tribromo-benzenes.[17] But in choosing these particular sets of isomers to work with, he was guided purely by considerations of convenience. Had he chosen the dinitro- and trinitro-benzenes or the dimethyl-tetrachloro- and trimethyl-trichloro-derivatives instead, the demonstration might (for experimental reasons) have been much more difficult, but the results would have been the same, because the relations investigated are type properties independent of the specific nature of the univalent substituents involved.

Reasoning quite analogous to that of Körner has been applied repeatedly to the solution of problems in structural and stereo-chemistry—often with conspicuous success. It needs no further argument to prove that the relations involved are always type properties. In many cases they suffice to identify uniquely each one of the compounds concerned, and even where the identification is not unique, they serve to limit the choice of a formula to be assigned to any one compound. But curiously enough these type properties do not appear to have been named.[18] They will be referred to hereafter in this paper as the genetic relations between adjacent sets of univalent substitution isomers.

Other Type Properties.—The type properties so far enumerated do not complete the list of all such properties known. If the class of isomers to be enumerated contains skeletal isomers, but the division into skeleton and univalent substituents is not subjected to the restrictions mentioned on p. 1038, certain other isomer numbers are obtained, which do not correspond to any common method of chemical classification, but which are nevertheless type properties of the molecules involved.

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[17] Körner: Gazz., 4, 305 (1874).

[18] Holleman in his "Textbook of Organic Chemistry," p. 504 et seq. (1920) speaks of "Korner's principle" and refers to the "absolute" determination of the ortho, meta and para positions by its means. J. B. Cohen in his "Organic Chemistry," Part II, p. 430 et. seq. (1928) uses the same terminology. There is however no explicit statement that the type of reasoning is quite general and by no means restricted in its application to the derivatives of benzene. For instance, of the five truxillic acids, only one should yield two diameric monoanilides, and the isomer in question is thus uniquely identified by this fact. (See Stoermer: Ber., 57, 18 (1924)). The word "absolute" has been overworked and should be avoided where possible.

If the molecule is divided into skeleton and substituents in such a way that some or all of the substituents are polyvalent, again certain isomer numbers which are type properties are obtained. In particular classes of compounds (for example the spiro compounds and the complex molecules derived from cobalt, chromium, etc.) this matter of polyvalent substitution isomerism is of great importance. It lies outside the scope of the present paper but does not appear to offer any additional sort of difficulties and is also a problem in permutation groups. Thus it should prove amenable to treatment by methods similar to those developed in subsequent sections of this article. Possibly it may be discussed more fully at some later time.

Beyond the type properties mentioned, no others are known to the authors of this paper. Those listed have one important characteristic in common. They are all pure numbers; and it will be shown that this characteristic of all these type properties is a fact of great significance.

Problems to be Considered.—Since attention is to be confined from now on to univalent substitution isomerism, the five type properties connected with isomerism of this sort are here recalled. They are

(1) The value of $N_V(p)$.

(2) The value of $N'_V(p)$.

(3) The value of $N''_V(p)$.

(4) The number of members of each of the $N''_V(p)$ structurally isomeric subsets of $S_V(p)$.

(5) The genetic relations between adjacent $S_V(p)$s.

The mathematical machinery for dealing with isomers of the three classes and properties of the sorts mentioned is next developed.

II. Determination of $Z_G(p)$

The Group G and its Induced Groups $H_G(p)$.—Any class consisting of d individuals determines definite classes of certain other entities such as unordered or ordered pairs; unordered, partially ordered, or completely ordered triples;[19] ordered pairs of unordered pairs, etc. In fact it is vital to the following discussion that to every value of (p) there corresponds a class of such entities. The table lists some examples, together with the number of entities in each class and the partition with which each class of entities is associated.

But although there is a class of entities corresponding to every value of (p), the converse is not true in the sense intended. For example, the class of unordered pairs of totally distinct unordered pairs, the number of which is

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[19] As unordered pairs *(ab)* and *(ba)* are identical; as ordered pairs they are not. The six forms

(abc)	*(acb)*	*(bac)*	*(cab)*	*(bca)*	*(cba)*
I	II	III	IV	V	VI

are identical as completely unordered triples; as completely ordered triples they are all different. Considered as triples ordered only as to *(a)*

I and II are identical.
III and IV are identical.
V and VI are identical.

The three pairs are however different from one another.

$\frac{d!}{(d-4)!\,2!\,2!\,2!}$, is not the class belonging to any partition in the sense of the general definition following. Moreover, the use of special names for the entities is superfluous, since every class of the sort here needed is uniquely defined by a particular value of (p) and may therefore be called simply the class belonging to (p).

For an arbitrary partition $(d_1, d_2 \ldots . d_t)$, the correspondence is fixed as follows. If d things are assigned to d places, there will be d! distinct assignments, provided the d things are individually distinguishable. This corresponds to the partition $(1,1 \ldots . 1,1)$. But if, of the d things, d_1 are alike of one kind, d_2 alike of a second kind, and so on, the number of distinguishable assignments is $\frac{d!}{d_1!\,d_2! \ldots . d_t!}$, and these constitute the class of entities belonging to the partition $(d_1,d_2 \ldots . d_t)$. It will be seen however that the placing of the last set of d_t things is determined by the placing of the other sets—hence the fitness of the special names mentioned above.

Entity	Partition	Number
Unordered d-tuples	(d)	$\frac{d!}{d!} = 1$
Individuals	$(d-1,1)$	$\frac{d!}{(d-1)!\,1!} = d$
Unordered pairs	$(d-2,2)$	$\frac{d!}{(d-2)!\,2!} = \frac{d(d-1)}{2}$
Ordered pairs	$(d-2,1,1)$	$\frac{d!}{(d-2)!\ 1!\,1!} = d(d-1)$
Unordered triples	$(d-3,3)$	$\frac{d!}{(d-3)!\,3!} = \frac{d(d-1)\ (d-2)}{6}$
Partially ordered triples	$(d-3,2,1)$	$\frac{d!}{(d-3)!\,2!\,1!} = \frac{d(d-1)\ d-2)}{2}$
Completely ordered triples	$(d-3,1,1,1)$	$\frac{d!}{(d-3)!\,1!\,1!\,1!} = d(d-1)\ (d-2)$
Ordered pairs of totally distinct unordered pairs	$(d-4,2,2)$	$\frac{d!}{(d-4)!\,2!\,2!} = \frac{d(d-1)\ (d-2)\ (d-3)}{4}$
Completely ordered d-tuples	$(1,1 \ldots . 1,1)$	$\frac{d!}{1!\,1!\,1! \ldots 1!\,1!\,1!} = d(d-1) \ldots (2)(1)$

A permutation of the d places determines a corresponding or "induced" permutation of the various assignments belonging to any single partition. It is clear, therefore, that any group G of permutations on the places induces a determinate group $H_G(p)$ of permutations on the class of entities belonging to the partition (p). The following table lists some of these groups which match classes of entities in the preceding table. (See Note C.)

Group	Partition	Degree
$H_G(d)$	(d)	$\frac{d!}{d!} = 1$
$H_G(d-1,1)$	$(d-1,1)$	$\frac{d!}{(d-1)!\,1!} = d$
$H_G(d-2,2)$	$(d-2,2)$	$\frac{d!}{(d-2)!\,2!} = \frac{d(d-1)}{2}$
$H_G(d-2,1,1)$	$(d-2,1,1)$	$\frac{d!}{(d-2)!\,1!\,1!} = d(d-1)$
$H_G(1,1\ldots\ldots 1,1)$	$(1,1\ldots\ldots 1,1)$	$\frac{d!}{1!\,1!\ldots\ldots 1!\,1!} = d(d-1)\ldots\ldots(2)$ (1)

Sets of Transitivity.—Every such induced group has a certain number $Z_G(p)$ of sets of transitivity. The symbol $Z_G(d_1,d_2,\ldots d_t)$ will be used to mean the number of sets of transitivity in the group $H_G(d,d_2\ldots d_t)$ which is a group of degree $\frac{d!}{d_1!\,d_2!\ldots.d_t!}$ induced by the group G (of degree d) for the partition $(d_1,d_2\ldots d_t)$. If all the q(d) values of (p) be considered in connection with any group G, there results a set of q(d) numbers which may be called a complete set of $Z_G(p)$s. One of these values of $Z_G(p)$ is, however, of a peculiar nature. The partition (d) induces a group H(d) which is always of degree one, no matter what G may be. So H(d) is always the identity and Z(d) is always unity.

Determination of $Z_G(p)$ by Direct Enumeration.—If G and (p) are known, a method of direct enumeration will theoretically determine $Z_G(p)$ in all cases. This method is illustrated by the following example in which (p) is (6,2), and the group G is generated by the operations

(1) *abcd.efgh* and (2) *ae.bh.cg.df*

Let a single letter be assigned to each of the 28 (= 8 × 7/2) unordered pairs of letters in the set *a* .... *h* as follows:

ab = A
bc = B
cd = C
ad = D
eh = E
ef = F
fg = G
gh = H

ac = I
bd = J
eg = K
fh = L
ae = M
bf = N
cg = O
dh = P

af = Q
bg = R
ch = S
de = T
ag = U
bh = V
ce = W
df = X

ah = Y
be = Z
cf = A′
dg = B′

Then the generators (1) and (2) in the group G of degree 8 become in the group $H_G(6,2)$ of degree 28

(1) ABCD.EFGH.MNOP.QRST.UVWX.YZA′.B′.IJ.KL

(2) AE.BH.CG.DF.NP.QT.RS.UW.YZ.A′B′.IK.JL

These two operations generate a group $H_G(6,2)$ which belongs to a class of groups expressible in the Cayley notation as follows:

$$\{[(ABCDEFGH)_8(MNOP.QRST.UVWX.YZA'B')_8]_{1:1}(IJKL)_4\}_{2:1}$$

Every group of this class has 6 sets of transitivity, and therefore $Z_G(6,2)$ is 6, where G has the significance assigned to it on the previous page.

A Formula for $Z_G(p)$.—There is never any theoretical difficulty in determining $Z_G(p)$ by such enumeration, but it may readily be seen that for large values of d and the more complex values of (p) the task becomes insufferably tedious. It is therefore important to have a more expeditious way of calcutaing this value. Such a method is to be found in an adaptation of the well known character theorem of Frobenius, which states that if L be the sum of the letters left invariant by the individual operations of a permutation group G of order g and degree d, then the number of sets of transitivity Z_G is equal to L/g.

If any partitition of d be written out in full and all the integers equal to unity omitted, the resulting set of integers represents a type (t) of operation which may occur in a permutation group of degree d. Conversely every operation of a permutation group has a determinate type in this sense. For instance where d is 8, the operation *abcdef.gh* is of type (6,2); the operation *abc.def* is of type (3.3); etc. According to this definition, the identity operation is unique in that its type is represented by a vacuous set of integers no matter what the degree of the group, and that it is the only operation of this type.

Let K(t) be the number of letters left invariant in a group G of degree d by an operation of type (t); and let n_t be the number of operations of type (t) in G. Then

$$L = \sum_t n_t K(t)$$

where the summation is in respect to all types (t) of operation in G. Hence

$$Z_G = \frac{\sum_t n_t K(t)}{g}$$

Where (p) is (d−1,1) and the group G is the group on the individuals, the formula becomes

$$Z_G(d-1,1) = \frac{\sum_t n_t K(t)}{g}$$

which is the Frobenius theorem in its ordinary form.

To adapt the formulation of this theorem to any partition (p) other than (d−1,1), it is necessary to have, not the number of individuals left invariant by an operation of type (t), but the number of invariant entities of the kind associated with the partition (p). In the general case the theorem is

$$Z_G(p) = \frac{\sum_t n_t K(p,t)}{g} \qquad \text{(A)}$$

whenever the induced group G(p) is simply isomorphous with the group G(d − 1,1). It is probable though still unproven that (except where (p) = (d) and G(p) is the identity) this simple isomorphism always occurs, inasmuch as the results calculated by formula (A) have been compared in a large number of cases with those obtained by the process of direct enumeration, and no discrepancy has been found.

Clearly the heart of the problem of determining $Z_G(p)$ for any G and for any value of (p) lies in the determination of the sets of values of K. By induction, an empirical method of computing these has been found. It is as follows.

If the sum of the integers in (p) is d, and the sum of the integers in (t) is e, then d − e is either 0 or a positive integer $\leqq$ d. If the integers in (t) are subtracted from those in (p) in any particular way, there is obtained a set of remainders

$$R_a = a_1, a_2 \ldots\ldots\ldots a_f \text{ such that}$$
$$a_1 + a_2 \ldots\ldots\ldots + a_f = d - e$$

If the subtraction is carried out in all possible ways, a number of sets of remainders $R_a, R_b \ldots\ldots\ldots R_f$ are obtained. And, if the following definitions are adopted

$$R_a! = a_1!\,a_2! \ldots\ldots a_f!$$
$$R_b! = b_1!\,b_2! \ldots\ldots b_f! \text{ etc.}$$

then
$$K = \frac{(d-e)!}{R_a!} + \frac{(d-e)!}{R_b!} + \ldots\ldots + \frac{(d-e)!}{R_f!}$$

The first special cases under this general formula which need particular attention are those where at least one integer in the set R_a has a negative value. If a_1 is a negative integer,

$$a_1! = \infty$$
$$R_a! = \infty$$

and
$$\frac{(d-e)!}{R_a!} = 0$$

Hence if (for any given value of (t) and (p)) every R contains at least one negative integer, then K is 0. If only certain Rs contain negative integers, then it is sufficient to consider only those which do not, because those containing negative integers have no effect on the value of K.

The special case of the identity comes under the general scheme, provided it is understood that a vacuous set of integers can be subtracted in only one way. In this case, the only R is $d_1, d_2 \ldots . d_f$ and $K = \dfrac{d!}{d_1!\,d_2! \ldots . d_f!}$

Where d − e = 0, every R which contains no negative integers is of the form 0, 0 .... 0, and since $\dfrac{0!}{0!\,0! \ldots\ldots\ldots 0!} = 1$

$$K = \frac{0!}{R_a!} + \frac{0!}{R_b!} + \ldots . + \frac{0!}{R_f!} = f$$

This method of computing K is very nearly automatic. The main difficulty is to be sure that the subtraction is carried out just once in every way which leads to no negative remainders. One means of attaining this end is to assign a fixed order to the integers in the minuend, and to index the identical integers in the subtrahend. Two examples illustrate the proper procedure.

Example I. $(p) = (3,3,1)$ $(t) = (3,2)$ $d-e = 3$

$$\begin{array}{ccc} 3 & 3 & 2 \\ 3 & 2 & \\ \hline 0 & 1 & 2 \end{array} \qquad \begin{array}{ccc} 3 & 3 & 2 \\ 3 & & 2 \\ \hline 0 & 3 & 0 \end{array} \qquad \begin{array}{ccc} 3 & 3 & 2 \\ 2 & 3 & \\ \hline 1 & 0 & 2 \end{array} \qquad \begin{array}{ccc} 3 & 3 & 2 \\ & 3 & 2 \\ \hline 3 & 0 & 0 \end{array}$$

$$K = \frac{3!}{3!} + \frac{3!}{3!} + \frac{3!}{2!} + \frac{3!}{2!} = 1 + 1 + 3 + 3 = 8.$$

Example II. $(p) = (4,2,2)$ $(t) = (2,2)$ $d-e = 4$

$$\begin{array}{ccc} 4 & 2 & 2 \\ 2_1 & 2_2 & \\ \hline 4-2_1 & 2-2_2 & 2 \\ 2 & 0 & 2 \end{array} \qquad \begin{array}{ccc} 4 & 2 & 2 \\ 2_1 & & 2_2 \\ \hline 4-2_1 & 2 & 2-2_2 \\ 2 & 2 & 0 \end{array} \qquad \begin{array}{ccc} 4 & 2 & 2 \\ 2_2 & 2_1 & \\ \hline 4-2_2 & 2-2_1 & 2 \\ 2 & 0 & 2 \end{array}$$

$$\begin{array}{ccc} 4 & 2 & 2 \\ 2_2 & & 2_1 \\ \hline 4-2_2 & 2 & 2-2_1 \\ 2 & 2 & 0 \end{array} \qquad \begin{array}{ccc} 4 & 2 & 2 \\ & 2_1 & 2_2 \\ \hline 4 & 2-2_1 & 2-2_2 \\ 4 & 0 & 0 \end{array} \qquad \begin{array}{ccc} 4 & 2 & 2 \\ & 2_2 & 2_1 \\ \hline 4 & 2-2_2 & 2-2_1 \\ 4 & 0 & 0 \end{array}$$

$$\begin{array}{ccc} 4 & 2 & 2 \\ 2_1 + 2_2 & & \\ \hline 4-2_1-2_2 & 2 & 2 \\ 0 & 2 & 2 \end{array}$$

$$K = \frac{4!}{2!\,2!} + \frac{4!}{2!\,2!} + \frac{4!}{2!\,2!} + \frac{4!}{2!\,2!} + \frac{4!}{2!\,2!} + \frac{4!}{4!} + \frac{4!}{4!}$$
$$= \frac{5 \times 4!}{2!\,2!} + \frac{2 \times 4!}{4!} = 5 \times 6 + 2 \times 1 = 32$$

By this method, the full set of values of K which correspond to any given d may be computed. When such a set has been completely evaluated, all the values of $Z_G(p)$ according to formula (A) may be determined for any group G of degree d. Table I gives all the values of K for $d < 11$; Table II gives all the values of $Z_G(p)$ for $d < 7$. See pp. 1072 to 1079.

No general proof has yet been found that this method of computation always yields the correct value of K, but in every case investigated, the number thus calculated corresponds to the value for K obtained by direct enumeration. Moreover it is clear that any formula which gave a fractional value for any single $Z_G(p)$ would be condemned at once; and the fact that formula (A) has always given integer values when K is computed in the manner described is evidence in favor of both the formula and the method of determining K.

The Group Restriction.—In the table for the values of $Z_G(p)$ each column represents a complete set of $Z_G(p)$s. It will be seen that for every value of d, the integers in the column of the group of order one are the largest integers in the table for their respective values of (p). Aside from this limitation, there is no obvious restriction on the integers which occupy the other places in the table. There is, for example, no evident rule as to the number of times any particular integer may be repeated. Where d is 5, the number of sets of integers which satisfy the above limitation is

$$5 \times 10 \times 20 \times 30 \times 60 \times 120 = 216 \times 10^6$$

Of these two hundred and sixteen million possibilities, all but nineteen are excluded by the group restriction on the permutations. Where d is 4, the corresponding fraction is 11 in 6912. And since q(d) increases rapidly with d, it is probable that (even though the number of groups of degree d also increases with d), the fraction in question rapidly becomes smaller as d becomes larger.

III. Molecules and Permutation Groups

Connection between Molecules and Permutation Groups.—If a molecule be divided into a skeleton V and d univalent substituents, sets of values for $N_V(p)$, $N'_V(p)$ and $N''_V(p)$ may be experimentally determined, complete as far as the difficulties in the preparation of the substances will permit. The all important fact which serves to link the data of chemistry with the purely mathematical considerations outlined in the previous section is that every set of $N_V(p)$s, $N'_V(p)$s or $N''_V(p)$s is identical (or at least compatible) with the set of $Z_G(p)$s for some permutation group of the same degree d. In the whole mass of isomerism data there does not appear to be one well-proven exception to this rule. The chance that this agreement for any single skeleton may be accidental is negligible, as is indicated by the very small fractions given above. Hence the assumption that at least one permutation group G can be associated with every given skeleton V, appears to be about as well justified as any generalization based on experimental evidence.

Since there is only one type of compound defined by a skeleton V and the partition (d), it is a matter of indifference whether G be thought of as associated with the skeleton V or with any molecule determined by V and (p) = (d). That is to say, the group of the six carbon atom ring of benzene may equally well be called the group of benzene, C_6H_6, or of hexachloro-benzene, C_6Cl_6. Consequently, hereafter, the group G will be spoken of indiscriminately as the group of the skeleton V, or as the group of a parent substance determined by V and (p) = (d). Anyone trained in organic chemistry will probably find it more familiar to think of the d like substituents (where (p) = (d)) as being all hydrogen atoms, since it is customary to regard hydrocarbons as the parent substances from which substitution products are derived.

Agreement or Compatibility of Numerical Data.—What is meant by the agreement or compatibility of a set of $Z_G(p)$s with a set of $N_V(p)$s may be illustrated by use of the table for degree four.

$$\left.\begin{array}{ll} Z_G(4) & = 1 \\ Z_G(3,1) & = 1 \\ Z_G(2,2) & = 3 \\ Z_G(2,1,1) & = 3 \\ Z_G(1,1,1,1) & = 6 \end{array}\right\} \text{is a complete set of } Z_G(p)\text{s where } G \text{ is } (abcd)_4$$

$$\left.\begin{array}{ll} N_V(4) & = 1 \\ N_V(3,1) & = 1 \\ N_V(2,2) & = 3 \\ N_V(2,1,1) & = 3 \\ N_V(1,1,1,1) & = 6\text{[20]} \end{array}\right\} \text{is a complete set of } N_V(p)\text{s where the skeleton } V \text{ consists of two carbon atoms united by a double bond.}$$

Ethylene, C_2H_4, is one example of a substance derived from this skeleton when (p) is (4); tetrachloro-ethylene, C_2Cl_4, is another. The substances derived from this skeleton when (p) has any other value may therefore be thought of as substitution derivatives of ethylene (or tetrachloro-ethylene).

Examination of the table containing all groups of degree four shows that the two equations $N_V(3,1) = 1$ and $N_V(2,2) = 3$ taken simultaneously agree respectively with the values of $Z_G(3,1)$ and $Z_G(2,2)$ for no other group beside $(abcd)_4$. The fact that for the skeleton in question $N_V(2,1,1)$ is 3 agrees with the value of $Z_G(2,1,1)$ for the same group. But if, as matter of experiment, $N_V(2,1,1)$ for the skeleton under consideration were 2, this fact would still be compatible with the group requirement though no longer in agreement with it. Such a state of the experimental data might mean that one of the theoretically possible substitution derivatives of ethylene had never been prepared—due to inadvertence, lack of interest, or experimental difficulties. But if, for the same skeleton, $N_V(2,1,1)$ were found experimentally to be 4, this fact, taken in connection with the previously established values of $N_V(3,1)$ and $N_V(2,2)$ would not be compatible with any group of degree four. If $Z_G(3,1)$ is 1, then $Z_G(2,1,1)$ cannot be 4 and vice versa. As already stated, throughout the range of chemistry no such data are known. It is always possible to find a group which is at least compatible with the experimental facts.

The Determination of Isomer Numbers and Molecular Groups.—The association of at least one permutation group with every molecular skeleton in the manner just described is attended with very wide consequences. It gives in terms of a permutation group $H_G(p)$ the mathematical analogue of any set $S_V(p)$ of isomers determined by the skeleton V and the partition (p). Furthermore $Z_G(p)$, the number of sets of transitivity in $H_G(p)$, is the same as $N_V(p)$, the number of isomers in $S_V(p)$; and so any method of calculating $Z_G(p)$ becomes a method of calculating $N_V(p)$. This means that formula (A)

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[20] As a matter of fact, no case where the six isomers required by the partition (1,1,1,1) have all been prepared has been found in the literature. For the case where the four different substituents are the hydrogen and bromine atoms and the methyl and carboxyl radicals, Beilstein lists five isomeric forms. The β bromo-isocrotonic acid has apparently never been prepared. But since the α and β forms of both chloro-crotonic and chloro-isocrotonic acids are known (vide Beilstein), the number six may be considered to be sufficiently well demonstrated.

(p. 1045) is a formula for calculating the number of isomers in any set $S_V(p)$ where the group of the skeleton is known. Conversely, there arises the possibility of reversing formula (A) and determining the group G from a complete set of $N_V(p)$s. Combining these two processes, it might be possible to determine G from certain experimentally known values of $N_V(p)$, and then to use this value of G to calculate the other values of $N_V(p)$. The values thus calculated could be compared with experimental results and would thus serve as a check on the correctness of the determination of G.

In exactly the same way $H_G'(p)$ and $Z_G'(p)$ are associated respectively with $S'_V(p)$ and $N'_V(p)$; also $H_G''(p)$ and $Z_G''(p)$ are associated respectively with $S''_V(p)$ and $N''_V(p)$. Hence formula (A) may be used in like fashion to calculate $N'_V(p)$ and $N''_V(p)$; G′ and G″ might also be determined from a sufficient number of values of $N'_V(p)$ and $N''_V(p)$ respectively. In the succeeding sections of this paper, these various operations will be discussed in greater detail.

Group and Configuration.—But the most important consequence of the association of a permutation group with a molecule is the light which this association throws on the so-called configuration of the molecule in question—that is on the space relations of its component atoms. Every geometrical configuration consisting of d points which are subject to stipulated relations of invariance determines a permutation group of degree d on these points. But it is not true that an assembly of d points and a permutation group of degree d on these points determines a space configuration for the assembly in question. In the first place, many permutation groups are compatible with a number of different space configurations. But what is more important, geometrical configurations are only one of a variety of ways representing or illustrating permutation groups. In fact, such a group has much the same relation to a space configuration as the mathematical law of inverse squares has to the physical laws of gravitation (Newtonian form), the Coulomb law of electrostatic attractions and repulsions, the law of the attractions and repulsions of magnetic poles, etc.

Suppose that a system be composed of two bodies, and suppose that an attractive force inversely proportional to the square of their distance from one another be known to exist between them. In default of further information, no decision as to the gravitational, electrostatic or magnetic nature of the force is justified. Nor can any item in the behavior of the system, the mathematical analogue of which is inherent in the abstract law of inverse squares be used to determine the physical nature of the force in question.

The mathematical analogue of $N_V(p)$ is $Z_G(p)$—a property not exclusively of the space configuration of the molecule, but of a permutation group on the univalent substituents. And all suitable space configurations as a class give only one out of various possible modes of illustrating such a group. For this reason, no inference as to the space configuration of the skeleton or of the molecule can be drawn simply from a value of $N_V(p)$ or even from a complete set of $N_V(p)$s. It is true that a space configuration (rigid or non-rigid) is likely to be available for use as an illustration of the permutation group in question; it is true that a geometrical diagram is usually the most convenient method of plotting the data; but the fact that the diagram is geometrical does not imply that the relations plotted are space relations. To assume that the relations are space relations cannot be in conflict with the known values of $N_V(p)$ (which are properties of the group), but neither is the special assumption justified by these stated facts. And the continued adherence to a particular mode of representation, instead of clarifying the situation, is apt to result in confusion between the properties of the phenomena observed and the properties of the particular method of representation adopted. Various instances where the group of the molecule throws more light on its properties than does its so-called configuration will be pointed out in the present paper.

IV. Determination and Applications of G and $N_V(p)$

Calculation of the Number of Univalent Substitution Isomers.—$N_V(p)$ has been defined as the number of univalent substitution isomers determined by the skeleton V and the partition (p), taking account of structural isomerism and stereo-isomerism, both diameric and enantiomorphous. It has already been shown (see preceding section) that, since every skeleton V is associated with a group G, and since each value of $N_V(p)$ is identical with the corresponding value of $Z_V(p)$, formula (A) (p. 1045) may be used to calculate the value of $N_V(p)$ wherever G is known. The formula as given is in its general form; but for certain special cases, it may be considerably simplified.

If every operation of a permutation group (except the identity) involves every letter of the group, then the "class" of the group is equal to its degree.[21] If a group of this kind is transitive, it must be regular; if it is intransitive and has n sets of transitivity, it must exhibit a 1:1......1:1 isomorphism between n regular groups on different sets of letters. For this reason, permutation groups of which the class is equal to the degree will hereafter be referred to as "multiregular" groups.

In multiregular groups, every type (t) of operation consists of identical integers and c is equal to d. Consequently, for such groups, every value of R must either contain negative integers or else it must be of the form 0,0....0,0. Under these conditions K(p,t) (for all values of (p) and (t)) is equal to the number of values of R which contain no negative integer. For this limited kind of groups, formula (A) reduces to the simplified form (B).

$$Z_G(d_1, d_2, \ldots, d_f) = \frac{1}{g}\sum_c \frac{n_c\left(\frac{d}{c}\right)!}{\left(\frac{d_1}{c}\right)!\left(\frac{d_2}{c}\right)!\cdots\left(\frac{d_f}{c}\right)!} \qquad \text{(B)}$$

where n_c is the number of operations of order c in G, and c is any common factor of g and $d_1, d_2 \ldots d_f$. Kauffmann's formulae for the numbers of substitution derivatives of quinoline, quinoxaline and naphthalene are special instances of this restricted formula. (See Note D).

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[21] For this technical use of the word class, see Miller, Blichfeldt, and Dickson: "Finite Groups," p. 47, (1916).

Another special form of (A) applies only where (p) is (1,1....1,1). This form (C) is

$$Z_G(1,1,\ldots,1,1) = \frac{d!}{g} \tag{C}$$

The significance of formula (C) will be brought out later on.

The Determination of the Group G.—The problem of determining G from certain values of $N_V(p)$ is usually of more interest than the converse problem just considered. This question may be resolved into a sequence of three:

(1) Does a complete set of $N_V(p)$s uniquely determine a permutation group G?

(2) If so, is the complete set of $N_V(p)$s necessary for this unique determination?

(3) If the complete set of $N_V(p)$s is not necessary for this purpose, how many and which values of $N_V(p)$ are sufficient?

The importance of the first question is self-evident. The reasons for the importance of the other two are as follows. For most skeletons, the value of $N_V(p)$ becomes fairly great as (p) becomes more and more complex. That is to say, in most of the chemically interesting cases, d!/g is large. Where G is $(abcdef)_{12}$ for example, Z (1,1,1,1,1,1) is 60; and to check this value experimentally would require the preparation and investigation of 60 different compounds. It will probably be readily admitted that such a program is usually out of the question. Consequently, it becomes important to know just how many and which values of $N_V(p)$ are sufficient to determine G uniquely. In order to be of practical interest, the sufficient values must lie among the less complex values of (p) where the values of $N_V(p)$ are small enough to permit of experimental verification.

The Significance of Literal Conformality.—The structure of formula (A) serves to indicate where part of the answer to the first question in the preceding paragraph is to be sought. From this formula, it is clear that if two or more permutation groups consist of equal numbers of operations of like type, they must give rise to identical sets of $Z_G(p)$s. And one part of the problem is therefore that of finding such sets of groups, if any exist. Permutation groups which satisfy the stated restriction must be isomorphous respectively with abstract groups which are either identical or conformal. But furthermore, they must exhibit an additional close relation as permutation groups. Apparently no name has ever been applied by mathematicians to sets of groups which exhibit this relationship. It is suggested that the members of such a set be called "literally conformal."

The mathematical questions connected with literal conformality need not be discussed in detail in this paper. It is hoped to treat them more adequately elsewhere. The proof that sets of literally conformal groups exist is easy, but a search of the tables shows that there are not many of degree less than 9. Probably the simplest set of this kind is the following pair.

I = $(abcd)_4(e)(f)$ consisting of the operations	II = $\{(ab)(cd)(ef)\}$pos consisting of the operations
1	1
ab.cd.e.f	*ab.cd.e.f*
ac.bd.e.f	*ab.ef.c.d*
ad.bc.e.f	*cd.ef.a.b*

Both of these groups of degree 6 consist of the identity and three operations of type (2,2). It is therefore clear that both must have the same set of $Z_G(p)$s. Consequently, if a molecule were associated with either one of them, it would be impossible to decide from the set of $N_V(p)$s alone which one was the group of the molecule in question.

The existence of literally conformal groups certainly shows that a complete set of $Z_G(p)$s is not always a means of uniquely defining a permutation group, and so the method loses some of its mathematical interest; but for chemistry it is nevertheless of great importance. The reason for this is not far to seek. The statement that with every molecular skeleton there is associated a permutation group is not likely to be at fault, but its converse is to say the least dubious. Indeed the very nature of chemical synthetic methods is such that it is hard to see how they could be used to prepare molecules to correspond to certain classes of permutation groups. The dicyclic groups, for example, seem to be chemically quite out of reach. It may perhaps turn out that the sets of literally conformal groups lie for the most part in that class of groups which is chemically inaccessible, and if this is so, then the method of determining G by its set of $Z_G(p)$s will be of much greater use chemically than it is mathematically. The existence of such a possibility calls attention to the urgent need for an abstract definition of the kind of groups which is chemically accessible. This subject is, however, beyond the scope of the present paper.

It has been shown that literal conformality is a sufficient condition for ambiguity in the determination of G from its set of $Z_G(p)$s. Whether it is a necessary condition or not is still unknown, since no cases of ambiguity which are not also literally conformal have so far been found. However, no member of any set of literally conformal groups yet discovered appears to be associated with a known molecular skeleton, so that, for the present, the whole question of literal conformality seems rather academic from the chemical point of view. For every molecular skeleton so far investigated, a complete set of $N_V(p)$s uniquely determines G.

The Sufficient Values of $N_V(p)$.—The second and third questions raised on p. 1052 are more easily disposed of. Mere examination of Table II reveals immediately that in many cases it is not necessary to have the complete set of $N_V(p)$s in order to determine G. But for the number of values of $N_V(p)$ sufficient in each particular case, no rule has yet been found. In the table for degree 5, the last value of $N_V(p)$ (counting from the top) necessary for the unique determination of G is underlined. The sufficient number varies from one to six.

The Group G of Benzene.—The method of determining G from part or all of a set of $N_V(p)$s and the value of the results obtained by this procedure may be illustrated by a few examples. Suppose that the skeleton in question is the six carbon atom ring of benzene. Then d is 6 and

(1) N (5,1) = 1
(2) N (4,2) = 3
(3) N (4,1,1) = 3

The degree of G is determined by d— in the present case 6. Since there are only 56 groups of degree 6, the choice of G is thus restricted. Equation (1) shows that G is a transitive group, and since only 16 of the groups of degree 6 are transitive, the choice of G is still further cut down. Of these 16 transitive groups, only 2, (*abcdef*)cyc and $(abcdef)_{12}$, agree with equation (2), and of these two only $(abcdef)_{12}$ is in agreement with equation (3). The group G of benzene is thus uniquely defined by these three equations, and further values of $N_V(p)$ may therefore be calculated from this value of G. The predicted values are

N (3 3) = 3
N (3,2,1) = 6
N (3,1,1,1) = 10
N (2,2,2) = 11
N (2,2,1,1) = 16
N (2,1,1,1,1) = 30
N (1,1,1,1,1,1) = 60

The experimental data are in agreement with the first four of these equations and compatible with the last three.[22]

The configuration of the benzene molecule has been a matter of discussion for the last fifty years and the question is still far from settled. But with only a small amount of isomerism data which has been almost unquestioned throughout that period, the group G of benzene can be quickly fixed beyond a shadow of doubt. And from this group may be derived much of the information which it was hoped to obtain from the configuration so long sought. Moreover the group may be used as a basis for certain conclusions which the configuration would tend to obscure. These statements will be substantiated in the course of the present paper.

The Group G of Ethane.—To give another example of the results which may be obtained by using the group G associated with a molecular skeleton it is instructive to consider the skeleton consisting of two carbon atoms united by a single bond. Here d is 6 and ethane is an example of the case where

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[22] In Richter's "Lexikon der Kohlenstoffverbindungen" (3rd Edition) there are listed ten isomeric forms of nitro-amino-toluene and eleven isomeric forms of dinitro-xylene. No case has been found where the full number of sixteen forms required by the partition (2,2,1,1) have all been prepared.

(p) = (d). No rigid configuration which accounts for the numbers of isomeric substitution derivatives of ethane has ever been found. In order to account for the experimental data, it has been assumed that free rotation about the single bond joining the two carbon atoms of the skeleton occurs in all these compounds. The fact that no rigid configuration has ever been found is however no proof that none exists. That proof can be obtained by use of the group G of ethane.

The equations

$$\begin{aligned} N\,(5,1) &= 1 \\ N\,(4,2) &= 2 \\ N\,(4,1,1) &= 3 \\ N\,(3,3) &= 2 \end{aligned}$$

uniquely determine the group G of ethane as $(abcdef)_{18}$. Now every permutation group is simply isomorphous with an abstract group, and the very limited classes of abstract groups which may be illustrated by rigid configurations have been defined beyond question. The group $(abcdef)_{18}$ is simply isomorphous with an abstract group which is not a member of any one of these classes. Hence as long as no change is made in the isomer numbers quoted, it will be mathematically impossible to find a rigid configuration for the ethane molecule.

The Group G of Cyclo-Pentamethylene.—Still another interesting application of the group concept is as follows. The attempt has recently been made[23] to develop from the symmetry system used by crystallographers a system applicable to substances in the fluid states. Such an attempt implies that axes of periods other than 1,2,3,4 or 6 can have no application to the subject matter of stereo-chemistry since they have none to the subject matter of crystallography.

The substance known as cyclo-pentamethylene has the empirical formula C_5H_{10}. If V is the five carbon atom ring of this molecule, then d is 10. Only one type of monosubstitution derivative of this compound has ever been obtained. The experimental data therefore justify the equation $N_V(9,1) = 1$. But if this is true, G is a transitive group of degree 10, and all such groups contain operations of order 5,[24] which are to be interpreted geometrically only as axes of period 5. Hence if no molecular configuration can contain an axis of period 5, there must be at least two univalent substitution isomers derived from the skeleton in question when (p) is (9,1). Until such a pair of separable isomers has been demonstrated, it would seem unwise to attempt to force stereo-chemistry into the narrow compass of a system restricted by the Haüy rational index law.

The G Groups of Homologous Series.—A fourth application of the group concept deserves mention at this point, but as it has not yet received thorough investigation, it cannot be given any adequate treatment in the present paper. Chemists have long been accustomed to classify molecules into

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[23] Weissenberg: Ber., 59, 1526 (1926).

[24] Cole: Quart. Jour. Math., 27, 40-42.

homologous series. The straight chain, saturated hydrocarbons, for example, form one clearly marked series of this kind; the primary, saturated, monohydric alcohols with unbranched chains form another. It is well known that in many such series the first member exhibits anomalies in behavior which differentiate it from all the other members. Formic acid, for instance, is the only straight chain saturated aliphatic acid which is a strong reducing agent.

Since each of the molecules in such a series is associated with a permutation group, it is natural to scan the groups of the series thus defined to see if they do not posses common properties analogous to the common properties of their respective molecules. Such properties common to the members of some of these series are instantly apparent. Moreover the groups often show anomalies to match those of the molecules themselves, for the first member frequently differs markedly from the others.

An example will probably make this matter clearer than a general discussion, and for this purpose the series of groups associated with the straight chain saturated hydrocarbons is as good an instance as any. There is a series of permutation groups (gh), $(gh.ij)$, $(gh.ij.kl)$, etc., each member of which is simply isomorphous with the abstract group of order 2. If the general symbol $_n(xy)$ be adopted for this series, then 2n will be the degree of any member group—n being any positive integer. The case $_0(xy)$ may be included in this scheme by defining it as the identity group.

Let G be the symbol for a series of groups G_1, G_2, etc. associated with a series of molecules. If the series of molecules be the straight chain saturated hydrocarbons, then G is $[(abcdef)_{18}\ {}_n(xy)]_{9:1}$. For ethane, n = 0; for propane, n = 1; for normal butane, n = 2; etc. That is

$$\begin{aligned} G_{\text{Ethane}} &= (abcdef)_{18} \\ G_{\text{Propane}} &= [(abcdef)_{18}(gh)]_{9:1} \\ G_{\text{Normal butane}} &= [(abcdef)_{18}(gh.ij)]_{9:1} \\ \text{Etc.} & \end{aligned}$$

This means that the G groups of all the straight chain saturated hydro-carbons except methane are simply isomorphous with the same abstract group—namely the group of order 18 generated as follows:

$$\begin{aligned} A^3 &= B^3 = C^2 = 1 \\ A_B &= A \\ A_C &= B \\ B_C &= A \end{aligned}$$

G_{Methane} is $(abcd)$pos which is of order 12 and consequently not simply isomorphous with the above abstract group.

If, in the symbol $N_V(p)$, V be taken as the properly chosen skeleton of any molecule which is a member of such a series as the one just mentioned, then (p) may be stated in terms of n. By formula (A), $N_V(p)$ may then be calculated. In this way there are obtained expressions which are functions of n and which are very similar to certain expressions developed by Kauffmann.[25]

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[25] Kauffmann: "Die Valenzlehre," pp. 130-134 (1911).

It is clear that the considerations mentioned are independent of the defining agreement as to the class of isomers to be enumerated, and so it is reasonable to expect that under like restrictions the values of $N'_V(p)$ and $N''_V(p)$ could also be calculated in terms of n. But little has yet been done in the way of developing these formulae, and at present it is merely desired to point out the possibility of such expansion without venturing any prediction as to the precise nature of the results to be attained thereby.

V. Determinations and Applications of G′ and $N'_V(p)$

Calculation of $N'_V(p)$.—$N'_V(p)$ has been defined as the number of univalent substitution isomers determined by the skeleton V and the partition (p), taking account of structural isomerism and diamerism, but neglecting enantiomorphism by counting each enantiomorphous pair as one individual. But every set of $N'_V(p)$s is in agreement or compatible with a set of $Z_G'(p)$s in exactly the same way that a set of $N_V(p)$s is in agreement or compatible with a set of $Z_G(p)$s. Hence all the primed symbols G′, $H_G'(p)$, $Z_G'(p)$, $S'_V(p)$ and $N'_V(p)$ have meanings exactly analogous to the unprimed symbols already employed. Moreover the formulae (A), (B) and (C) are independent of the defining agreement which fixes the class of isomers to be enumerated and determines the group; they are therefore as well applicable to the determination of $N'_V(p)$ as of $N_V(p)$. Also they may equally well be reversed and used for the determination of G′ from a sufficient number of values of $N'_V(p)$. In general the methods of determining G and the results obtained by the use of G are paralleled by a set of similar methods and results for G′.

The Relations of G′ and G.—The nature of G′ by itself may not be of much interest, but the comparison of G′ with G where V is constant is a matter of great importance. In the first place, since,

$$Z_G(p) = N_V(p) \text{ and } Z_G(p) = N'_V(p)$$

$$\text{then} \quad Z_G(p) - Z_G'(p) = N_V(p) - N'_V(p)$$

But $N_V(p) - N'_V(p)$ is the number of enantiomorphous pairs in $S_V(p)$. Its analogue, $Z_G(p) - Z_G'(p)$ is a property of the pair of permutation groups G and G′, and can therefore be discussed independently of any space configuration.

Inspection of all the particular cases studied has suggested a general proposition, namely, that the dyadic nature of the enantiomorphous relation E always limits the relations of G and G′ to two possibilities:

(a) $G = G'$ and $g = g'$

(b) G is a subgroup of G′ and $g = g'/2$.

Both of these possibilities need further discussion.

If $G = G'$ and $g = g'$, then $H_G(p) = H_G'(p)$, $Z_G(p) = Z_G'(p)$, $S_V(p) = S'_V(p)$ and $N_V(p) = N'_V(p)$ for all values of (p). This implies that there are no enantiomorphous pairs in $S_V(p)$; but here two explanations are possible.

(1) For all values of (p), every member x of $S_V(p)$ is such that there exists no substance y such that x E y.

(2) For all values of (p), every member x of $S_V(p)$ is such that there exists a substance y such that x E y, but y is not a member of $S_V(p)$.

If statement (1) holds true, then no substitution derivative of the parent substance is a member of an enantiomorphous pair. Ethylene is an example of such a parent substance. If statement (2) holds true, then every substitution derivative of the parent substance (A) is enantiomorphous with a compound derived by substitution from a different parent substance (B). The natural interpretation is that (A) and (B) are themselves enantiomorphous, and their skeletons may likewise be so considered. Dextro and laevo camphor are examples of such an enantiomorphous pair. Every univalent substitution derivative of dextro camphor is a member of an enantiomorphous pair, but no pair of enantiomorphs may be derived by substitution from dextro camphor. Every univalent substitution derivative of dextro camphor is a skeletal isomer of its enantiomorph derived from laevo camphor.

If G is a subgroup of G′ and $g = g'/2$, then since, according to formula (C)

$$Z_G(1,1\ldots.1,1) = d!/g \qquad \text{and} \qquad Z_{G'}(1,1\ldots.1,1) = d!/g'$$
$$Z_G(1,1\ldots.1,1) = 2Z_{G'}(1,1\ldots.1,1)$$

But (1,1....1,1) is the only value of (p) for which so simple a relation always holds.

The Group G′ of Ethane.—The use of the values of $N_V(p)$ and $N'_V(p)$ in connection with one another often simplifies the determination of both G and G′. For example, if V is a pair of carbon atoms united by a single bond

$$\begin{array}{llll} N\,(5,1) & = 1 \qquad\qquad & N'\,(5,1) & = 1 \\ N\,(4,2) & = 2 & N'\,(4,2) & = 2 \\ N\,(4,1,1) & = 3 & N'\,(4,1,1) & = 2 \\ N\,(3,3) & = 2 & N'\,(3,3) & = 2 \end{array}$$

These values of $N'_V(p)$ do not uniquely determine G′. The groups $(\pm abcdef)_{24}$, $(abcdef)_{36}$, $(abcdef)_{36}$, $(abcdef)_{48}$ and $(abcdef)_{72}$ all agree with the figures cited. But since the quoted values of $N_V(p)$ uniquely determine G as $(abcdef)_{18}$, G′ must be of order 36 and must contain $(abcdef)_{18}$ as a subgroup. The group $(abcdef)_{36}$, is the only group of degree 6 which fulfills these requirements, hence the other possibilities for G′ are excluded. It is true that these other groups may also be excluded by considering the more complex values of (p) and the $N'_V(p)$s associated with them, but the reasoning just given cuts down the amount of experimental data necessary for the unique determination of G′. The advantage of considering together the $N_V(p)$s and $N'_V(p)$s is therefore obvious.

The Group G′ of Benzene.—The procedure just outlined leads to some striking results where V is the six carbon atom ring of benzene. As has already been shown, the three equations

$$\begin{array}{ll} N\,(5,1) & = 1 \\ N\,(4,2) & = 3 \\ N\,(4,1,1) & = 3 \end{array}$$

uniquely determine G as $(abcdef)_{12}$. Suppose that $g = g'/2$. G' must therefore be a group of degree 6 and order 24 which contains $(abcdef)_{12}$ as a subgroup. Since it is well known that no such group exists, $g \neq g'/2$, and therefore $g = g'$. Hence $G = G'$ and enantiomorphism is impossible among univalent substitution isomers derived from one benzene. This may be explained in two ways. Either there is only one benzene, and no substitution derivative of it is a member of an enantiomorphous pair, or else there are two (skeletally isomeric) enantiomorphous benzenes, and every substitution derivative of either one is a member of a (skeletally isomeric) enantiomorphous pair. It is the first alternative which corresponds with the known facts. In short, for some univalent substitution derivatives of benzene to exhibit enantiomorphism while others do not is a mathematical impossibility as long as the values of $N_V(p)$ cited are not altered by experiment. This conclusion emerges very promptly as soon as the groups G and G′ of benzene are considered. It has successfully eluded many of those[26] who for over half a century have argued about the space configuration of this molecule.

Sets of Transitivity corresponding to Enantiomorphous Pairs.—Perhaps the most important result obtained by the simultaneous consideration of G and G′ is the identification of the pairs of sets of transitivity in $H_G(p)$ which correspond to the pairs of enantiomorphs in $S_V(p)$. The way in which this identification may be accomplished is illustrated by the case where V is the three carbon atom ring of cyclopropane. Here

$N(5,1) = 1 \qquad N'(5,1) = 1$

$N(4,2) = 4 \qquad N'(4,2) = 3$

These data[27] identify G as $(abcdef)_6$ and show that $G' \neq G$. Hence G' is of order 12 and contains $(abcdef)_6$ as a subgroup; it is therefore $(abcdef)_{12}$. Now $(abcdef)_6$ is generated by the operations *abc.def* and *ad.bf.ce*, and $(abcdef)_{12}$ results when $(abcdef)_6$ is extended by the operation *ad.be.cf*. If

$ab = A \qquad ae = D \qquad bd = G \qquad cd = J \qquad de = M$

$ac = B \qquad af = E \qquad be = H \qquad ce = K \qquad df = N$

$ad = C \qquad bc = F \qquad bf = I \qquad cf = L \qquad ef = O$

then $H_G(4,2)$ is generated by the two operations

(1) CHL.DIJ.EGK.AFB.MON and (2) HL.DJ.EG.AN.BM.FO. $H_G(4,2)$ is therefore of the type [(CHL.DIJ.EGK) all $(\text{AFBMON})_6$] 1:1. $H_G'(4,2)$ is generated by operations (1) and (2) and EJ.DG.IK.AM.BN.FO. and is therefore of the type [(CHL, all $(\text{DIJEGK.AFBMON})_{12}$] 1:2. Obviously it is the two sets (DIJ) and (EGK) in $H_G(4,2)$ which coalesce into the single set (DIJEGK) in $H_G'(4,2)$. Hence it is these two sets of transitivity (DIJ) and (EGK) which represent the enantiomorphous pair among the four isomers in $S_V(4,2)$. To decide which of these enantiomorphs is

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[26] LeBel: Bull., (2), 38, 98 (1882); Lewkowitsch: Ber., 16, 1576 (1883); J. Chem. Soc., 53, 781 (1888); Meyer and Lühn: Ber., 28, 2795 (1895).

[27] Beilstein lists four forms of cyclopropane dicarboxylic acid of which two are members of an enantiomorphous pair.

represented by (DIJ) and which by (EGK) is impossible, and similarly, if any pair of enantiomorphs is considered by itself, the distribution of formulae between the members of the pair is an arbitrary proceeding.

VI. Genetic Relations

Genetic Relations as Analogues of Group Properties.—The genetic relations between adjacent $S_V(p)$s have been shown to be type properties, and it is therefore of interest to inquire whether or not these properties, like the other type properties already discussed, have mathematical analogues inherent in the groups associated with the molecules in question, and are consequently independent of space configurations. Examples as good as any are the relations studied by Körner where the skeleton V is the carbon ring of benzene and the adjacent partitions are (4,2) and (3,3). In this case G is $(abcdef)_{12}$. $N_V(4,2)$ is 3 and $N_V(3,3)$ is 3.

If the operations of $(abcdef)_{12}$ are written out, first in the Cayley notation and then in a more explicit form, the following table is obtained.

Cayley Notation	Explicit Form
1	*a b c d e f*
abc.def	*b c a e f d*
acb.dfe	*c a b f d e*
ad.be.cf	*d e f a b c*
aecdbf	*e f d b c a*
afbdce	*f d e c a b*
ab.de	*b a c e f d*
ac.df	*c b a f e d*
bc.ef	*a c b d f e*
ad.bf.ce	*d f e a c b*
ae.bd.cf	*e d f b a c*
af.be.cd	*f e d c b a*

From the explicit form of the operations, it may be seen that the unordered pair *ad* is replaced successively by the unordered pairs *be* and *cf*. This means that the set

I = (*ad,be,cf*)

represents one set of transitivity in the group $H_G(4,2)$. Similarly

II = (*ae,bf,cd,bd,ce,af*) and
III = (*ab,bc,ac,de,ef,df*)

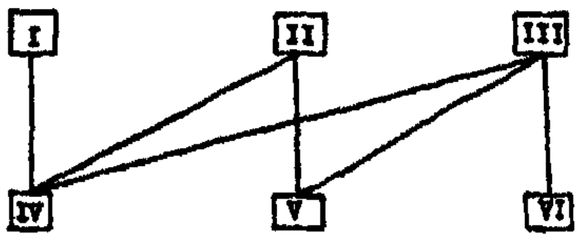
represent two other sets of transitivity in the same group. And since there are but fifteen unordered pairs, $Z_G(4,2)$ is 3.

In a like manner, the completely unordered triple *abd* is replaced by the completely unordered triples *bce, acf, ade, bef, cdf, abe, bcf, acd, adf, bed* and *cef*. Hence

IV = (*abd, bce, acf, ade, bef, cdf, abe, bcf, acd, adf, bed, cef*)

represents a set of transitivity in $H_G(3,3)$. Similarly
V = (*ace*, *abf*, *bcd*, *bdf*, *cde*, *aef*) and
VI = (*abc*,*def*)
represent two other sets of transitivity in the same group. This completes the list of 20 completely unordered triples, and so $Z_G(3,3)$ is 3.

The pairs of I appear only in the triples of IV; therefore I is adjacent to IV only. The pairs of II appear in the triples of IV and V but not in the triples of VI; hence II is adjacent to IV and V but not to VI. The pairs of III appear in the triples of IV, V and VI; hence III is adjacent to all three of these sets. These relations may be represented schematically by the following diagram. And it will be seen by reference to p. 1041 that the two diagrams are exactly analogous. So in this case at least, the adjacency relations between the sets of transitivity in $H_G(4,2)$ and $H_G(3,3)$ are the exact analogues of the genetic relations between the members of $S_V(4,2)$ and $S_V(3,3)$. And just as the genetic relations are sufficient to identify each one of the isomers, so the adjacency relations are sufficient to identify each one of the sets of transitivity.



If the unordered pairs are labelled as on p. 1059, the group $H_G(4,2)$ is of the type $[(\mathrm{CHL})\mathrm{all}(\mathrm{DIJEGK.AFBMON})_{12}]_{1:2}$ as was shown at that point. If the completely unordered triples are labelled in a like fashion as follows:

abc = A′ *acd* = E′ *adf* = I′ *bcf* = M′ *cde* = Q′
abd = B′ *ace* = F′ *aef* = J′ *bde* = N′ *cdf* = R′
abe = C′ *acf* = G′ *bcd* = K′ *bdf* = O′ *cef* = S′
abf = D′ *ade* = H′ *bce* = L′ *bef* = P′ *def* = T′

then the group $H_G(3,3)$ is generated by the two operations
(1) A′T′. B′P′G′H′L′R′. C′S′E′N′M′I′. F′Q′K′O′D′J′
(2) B′C′. P′I′. G′M′. H′N′. L′E′. R′S′. J′O′. F′K′
and is therefore of the type

$$\{[(B'P'G'H'L'R'C'S'E'N'M'I')_{12}(F'Q'K'O'D'J')_{12}]_{1:1}(A'T')\}_{6:1}$$

The genetic and adjacent relations just developed show that
(1) The set (CHL) represents I, the para compound.
(2) The set (DIJEGK) represents II, the ortho compound.
(3) The set (AFBMON) represent III, the meta compound.
(4) The set (B′P′G′H′L′R′C′S′E′N′M′I′) represents IV, the unsymmetric compound.
(5) The set (F′Q′K′O′D′J′) represents V, the vicinal compound.
(6) The set (A′T′) represents VI, the symmetric compound.

In the case just cited, it is clear that the mathematical analogues of the genetic relations between the sets of isomers are the adjacency relations between the groups. But there is nothing in the type of reasoning used which restricts the groups to which it may be applied. Hence the genetic relations are in general analogous to the adjacency properties of the groups, and therefore independent of space configurations.

Genetic Relations as Supplements for Sets of $N_V(p)$s.—These genetic relations, like the enantiomorphous relations previously discussed, help to reduce the number of values of $N_V(p)$ necessary for the determination of G. If (p_a) and (p_b) are two adjacent partitions, it may well be that $N_V(p_a)$ and $N_V(p_b)$ are in agreement with the corresponding $Z_G(p)$s for more than one group. Let two such groups be G_1 and G_2. Even though

$$Z_{G_1}(p_a) = Z_{G_2}(p_a) \text{ and } Z_{G_1}(p_b) = Z_{G_2}(p_b)$$

it is improbable that the adjacency relations between $H_{G_1}(p_a)$ and $H_{G_1}(p_b)$ will be the same as those between $H_{G_2}(p_a)$ and $H_{G_2}(p_b)$. And so if the genetic relations are worked out for $S_V(p_a)$ and $S_V(p_b)$, they may suffice to eliminate either G_1 or G_2. If the number of groups in agreement with all known values of $N_V(p)$ is large, such genetic relations may not be sufficient to identify G uniquely, but the number of possible groups is often considerably reduced.

As was mentioned in section IV, certain sets of literally conformal groups have been found, the members of which cannot be distinguished by complete sets of $Z_G(p)$s. It is interesting to note that in all cases so far investigated, each group of this kind has been found to be identifiable by the adjacency relations of the $H_G(p)$s. That is, so far as known, any permutation group may be uniquely identified, either by a sufficient number of values of $Z_G(p)$ alone, or else by these values considered in connection with the adjacency relations between the $H_G(p)$s. It seems probable, therefore, that it is possible with sufficient type data to define uniquely the group associated with any molecular skeleton.[28]

Taking the genetic and enantiomorphous relations together, it is frequently possible (as in the case cited in full) to establish the correspondence between each isomer in $S_V(p)$ and each set of transitivity in $H_G(p)$, except that only the pair of sets corresponding to a pair of enantiomorphs may be determined. It is not always possible to work out so complete a system of correspondence, but in every case yet investigated a large number may easily be found.

Cis and Trans Derivatives of Ethylene.—It is instructive to examine a case where reasoning of this sort is inadequate, in order to illustrate the fate of problems in which conclusions drawn from type properties are insufficient for a unique solution. If the skeleton V consists of two carbon atoms united by a double bond, then

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[28] It by no means follows from this statement that G uniquely determines V. For example, in the dioxan and dithian molecules, if V is so chosen that d is 8, then G_{Dioxan} is identical with G_{Dithian}. And other instances where widely differing values of V determine the same G might be cited. The relations of the different skeletons which give rise to the same G form an intricate problem in connexity.

$N(3,1) = 1$	$N'(3,1) = 1$	$N''(3,1) = 1$
$N(2,2) = 3$	$N'(2,2) = 3$	$N''(2,2) = 2$
$N(2,1,1) = 3$	$N'(2,1,1) = 3$	$N''(2,1,1) = 2$
$N(1,1,1,1) = 6$	$N'(1,1,1,1) = 6$	$N''(1,1,1,1) = 3$

These data determine both G and G′ as $(abcd)_4$ and G″ as $(abcd)_8$. Since there are no two enantiomorphous skeletons which correspond to the above definition of V, enantiomorphism is lacking among the substitution derivatives of ethylene.

The problem to be solved is the correlation of each one of the three isomers in $S_V(2,2)$ with one of the three sets of transitivity in $H_G(2,2)$. The group G is generated by the operations *ab.cd* and *ac.bd*; the operation *ac* extends this group $(abcd)_4$ to $(abcd)_8$ which is G″. Let

ab = A
ac = B
ad = C
bc = D
bd = E
cd = F

Then $H_G(2,2)$ is generated by the operations BE.CD and AF.CD; it is therefore the group [(AF)(BE)(CD)]pos. This group contains three sets of transitivity—which agrees with $N_V(2,2) = 3$. $H_G''(2,2)$ is generated by BE.CD, AF.CD, and AD.CF; it is therefore the group [$(AFCD)_8$pos(BE)]dim. This group contains only two sets of transitivity—in agreement with $N''_V(2,2) = 2$. These results indicate that one of the three isomers in $S_V(2,2)$ is related by structural isomerism with the other two which are stereo-isomers. And since these two are not enantiomorphs, they must be diamers. (BE) is the set of transitivity in $H_G(2,2)$ which corresponds to the structurally related isomer in $S_V(2,2)$; (AF) and (CD) correspond to the diameric pair.

The next step is to decide which member of this pair corresponds to (AF) and which to (CD). It has been shown that the relations of G and G″ are insufficient to establish the correspondence. Since G = G′, no help is to be obtained from enantiomorphism. Hence it is necessary to have recourse to the genetic relations.

A complete diagram of the genetic and isomeric relations between substitution derivatives of ethylene for all values of (p) is given below.

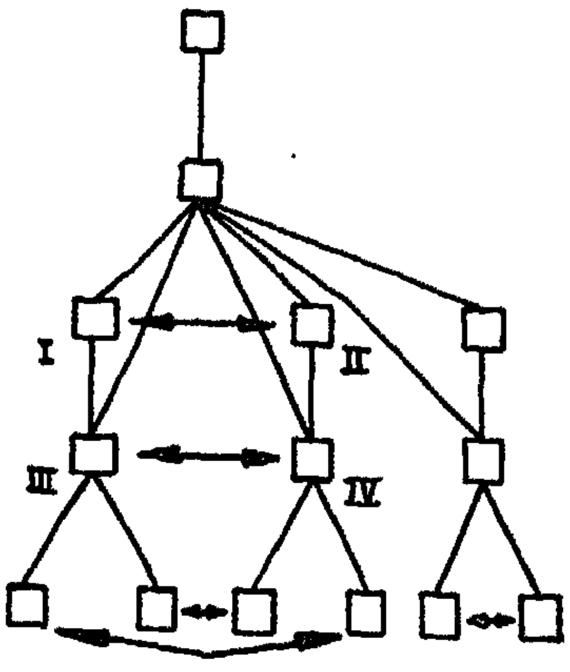
(p) = (4) N(p) = 1 N″(p) = 1

(p) = (3,1) N(p) = 1 N″(p) = 1

(p) = (2,2) N(p) = 3 N″(p) = 2

(p) = (2,1,1) N(p) = 3 N″(p) = 2

(p) = (1,1,1,1) N(p) = 6 N″(p) = 3



The presence of a horizontal double arrow indicates a diameric relation between two isomers; the absence of such an arrow indicates that the relation is one of structural isomerism. The two diamers under discussion are I and II, and the table shows at a glance that there is in it no genetic relation which serves to distinguish one of these isomers from the other.

Since the relations between G, G', and G'' also fail to differentiate these two substances, only one conclusion is possible. Such a pair of isomers cannot be distinguished by any type property now known. And the same is true of the diameric pair III, IV. This conclusion is entirely in agreement with experimental practice. Whenever diameric pairs of disubstitution derivatives of ethylene have been investigated, it has been necessary to fall back on the specific properties of the molecules in question in order to decide which one is the cis and which one the trans isomer.

The classic example of this sort of a pair of diamers is the case of maleic and fumaric acids. Here the decision is based on the relative tendency of the two dibasic acids to yield cyclic anhydrides. Of course this anhydride formation is a specific property of the two carboxyl groups. No decision on similar grounds is possible in the case of stilbene and iso-stilbene where no univalent substituents with ring-forming properties are present.

As to the value and permanence of conclusions based on such specific properties, it is sufficient to review the history of the maleic-fumaric acid question. This pair of acids was first thoroughly discussed in 1889 by Wislicenus,[29] who decided that maleic acid was the cis and fumaric acid the trans form. From that time on the discussion has continued. In 1926, Kuhn published a paper gravely questioning the correctness of Wislicenus's reasoning. His work called forth at least two controversial answers, to which he replied with new arguments supporting his previous publication.[30] A reasonable prediction is that argument on this subject will go on until the discovery of a type property which differentiates the two substances in question. It will then cease once and for all, just as argument about the ortho, meta and para positions ceased when Körner published his results in 1874.

VII. Structurally Isomeric Univalent Substitution Isomers

The Calculation of $N''_V(p)$.—The number of structurally isomeric sets of univalent substitution isomers determined by a given skeleton V and a given value of (p) has been defined as $N''_V(p)$. And just as a complete set of $N_V(p)$s or $N'_V(p)$s usually determines and is always compatible with a permutation group G or G', so in like manner a complete set of $N''_V(p)$s usually determines and is always compatible with a permutation group G''. Hence formulae (A), (B) and (C) can be used to calculate $N''_V(p)$ if G'' is known. These formulae can also be reversed (as in the preceding sections) and used to determine G'' from a sufficient number of values of $N''_V(p)$. $N''_V(p)$ again has its analogue in the properties of the group $H_{G''}(p)$, and is similarly independent of the space configuration of the molecule.

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[29] Wislicenus: Abhand. math. physik. Klasse sächs. Akad. Wiss., **14**, 1 (1889).

[30] Kuhn and Ebel: Ber., **58**, 919, 2088; Meisenheimer: 1491; Boeseken: 1470 (1925).

The Relations of G and G''.—The relations of G and G' to G'' (when V is constant) offer some fascinating and puzzling problems, most of which lie beyond the scope of the present paper. It is hoped to return to them in a later article. But one particular instance of such relations will be considered in some detail because it shows how the number of isomers in $S_V(p)$ which go to make up each one of the subsets in $S''_V(p)$ may be determined.

Where V is the three carbon atom ring of cyclopropane, $N_V(4,2)$ is 4 and $N''_V(4,2)$ is 2. One of the subsets in $S''_V(4,2)$ contains three of the isomers in $S_V(4,2)$; the other contains but one. For this skeleton

$N''(5,1) = 1$
$N''(4,2) = 2$
$N''(4,1,1) = 2$
$N''(3,3) = 2$
$N''(3,2,1) = 3$

These data[31] are in agreement with the idea that $G''_{\text{Cyclopropane}}$ is $(abcdef)_{48}$, a group of which $(abcdef)_6$ is a subgroup.[32] As stated on p. 1059, $(abcdef)_6$ (which is generated by *abc.def* and *ad.bf.ce*) is the group $G_{\text{Cyclopropane}}$. The operation *ad* extends $(abcdef)_6$ (=G) to $(abcdef)_{48}$ (=G''). On p. 1059 it was also shown that for the value of V here considered, $H_G(4,2)$ is of the type $[(\text{CHL.DIJ.EGK})\text{all}(\text{AFBMON})_6]_{1:1}$. Where (p) is (4,2), the extending operation *ad* becomes AG.BJ.DM.EN, and $H_G''(4,2)$ is of the type $[(\text{CHL})\ \text{all}(\text{CIJEGKAFBMON})_{48}]_{1:8}$. In other words, the effect of extending $H_G(4,2)$ to $H_G''(4,2)$ is to make the three sets of transitivity (DIJ), (EGK) and (AFBMON) coalesce into the single set (DIJEGKAFBMON). These three sets therefore represent the three isomers which are distinct as long as stereo-isomerism is taken into account, but which become identical when this form of isomerism is no longer considered. The fourth set (CHL) represents the isomer which retains its individuality even when stereoisomerism is disregarded and which is thus proved to be structurally isomeric with the other three.

Since (DIJ) and (EGK) have already been shown, p. 1059, to represent a pair of enantiomorphs, the relations developed are sufficient to permit the correlation of each one of the sets of transitivity in $H_G(4,2)$ with one of the isomers in $S_V(4,2)$, except that there is no means of deciding which one of the enantiomorphous pair is represented by (DIJ).

Reasoning of the sort here employed is independent of the nature of V and (p), and consequently whenever G and G'' are known, such reasoning may be used to determine the number of isomers in $S_V(p)$ which go to make

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[31] For $N''(4,1,1) = 2$ see Marburg: Ann., **294**, 131 (1897); also Kohn and Mendelewitsch: Monatsscheft., **42**, 241 (1921).
For $N''(3,3) = 2$ see Conrad and Guthzeit: Ber., **17**, 1186 (1884); also Perkin and Ing: J. Chem. Soc., **125**, 1816 (1924).
For $N''(3,2,1) = 3$ see Goss, Ingold and Thorpe: J. Chem. Soc., **123**, 3353 (1923); also Marburg: Ann., **294**, 112 (1897); also Staudinger et al.: Helv. Chim. Acta, **7**, 401 (1924).

[32] The other values of G'' which are in agreement with these data are excluded on grounds which will not here be discussed.

up each one of the subsets in $S''_V(p)$. Hence these numbers are again properties of the groups G and G″, and therefore independent of the space configuration.

VIII. Conclusions

The properties emphasized in this paper are the following:

(1) The number of univalent substitution isomers in the set $S_V(p)$ determined by a given skeleton V and a given value of (p).

(2) The number of enantiomorphous pairs in $S_V(p)$.

(3) The number of structurally isomeric subsets in $S_V(p)$.

(4) The number of members of $S_V(p)$ in each of the structurally isomeric subsets of $S_V(p)$.

(5) The genetic relations between adjacent $S_V(p)$s.

All these five properties have mathematical analogues inherent in the groups G, G′ and G″ and therefore need no consideration of space configuration. Since these complete the known list of type properties which have to do with univalent substitution isomerism, it may be stated that the known type properties related to such isomers cannot justifiably be used to determine the space configuration of the molecule in question. In view of the fact that the type properties mentioned are all expressed by pure numbers, this conclusion should occasion no particular surprise.

The great majority of space configurations in the chemical literature are, however, based principally on just these five properties. In fact, were the conclusions founded on such data eliminated, knowledge of molecular space configurations would be reduced to a small fraction of what is now supposed to be known. It would be necessary to rely entirely on specific properties for information in this field.

There are, it is true, certain theories based on the specific properties of molecules which bear on the matter of space configuration. Such are the Baeyer strain theory, the theory of steric hindrance, the dissociation theory of Bjerrum, the theories of dipole moments, band spectra, etc. These theories have been relied on to confirm (where they do not contradict) the evidence based on type properties. Whether it is possible to develop from such ideas alone a consistent system of molecular space configurations is a matter of individual opinion, since the question is certainly open to doubt.

If the term "configuration" (meaning space configuration) were to vanish from a large part of chemical theory, and the term "permutation group" were to take its place, such a change might well be regarded as a step forward. In the first place, it is possible to deduce from the permutation group most of what has customarily been deduced from the configuration. Secondly, whatever cannot be deduced from the permutation group cannot be deduced from the type properties of the molecule in question, or at least not from those type properties which have to do with univalent substitution isomerism. And since experience has shown that type properties have furnished a foundation for reasoning very much surer than that furnished by specific properties, it would be possible by use of the concept "permutation group" to distinguish certain parts of chemical theory which are relatively certain from others which are relatively questionable. Thirdly, by fixing attention on the permutation groups associated with a given molecule, it is possible in some instances to elicit from the facts more information than is obtainable by exclusive consideration of the space configuration usually attributed to the molecule in question.

Moreover, the use of permutation groups in place of space configurations would put an end to much of the confusion which has recently arisen in this field. For many years the determination of molecular space configurations lay in the hands of organic and inorganic chemists. The results which they obtained formed a system almost completely self-consistent and of very wide scope. But recently physicists, using the X-ray spectrograms of crystals, and physical chemists, using dipole moments, band spectra, etc., have entered the field; and the results obtained by the new methods are often at variance with those previously obtained under the guidance of stereo-chemical theories.

A way of escape from this dilemma is clear. If two independent investigators determine the space configuration of the same molecule under like conditions and arrive at contradictory results, at least one conclusion must be in error. Both may be. But if the same two investigators set out to determine the permutation group of the molecule in question and arrive at different results, it is entirely possible that both conclusions may be correct. A molecule is associated not with one but with many permutation groups. In the present article, the three which are most commonly considered by organic chemists (that is G, G′ and G″) have been discussed. No doubt there are many others. Which of these groups emerges upon investigation depends on various considerations among which are the definition adopted for the term "pure substance" and the defining agreement as to the class of isomers to be enumerated. In fact, every permutation group so determined is to be regarded as an aspect of the molecule under discussion. Occasionally two formally different aspects of one molecule may turn out to be the same (as in the case where G = G′), but such instances are the exception and not the rule. If two so-called configurations of one molecule arrived at by different methods turn out to be the same, the identity requires explanation. If they turn out to be different, this result is only what would usually be expected.

The definitions of pure substance, and the defining agreements as to the classes of isomers to be enumerated used (sometimes without explicit statement) by physicists and physical chemists are not synonymous with those customarily used (also for the most part without explicit statement) by organic chemists.[33] Hence it is not strange that the new results do not agree with those previously regarded as well established. If the claim is made that these new views add to the knowledge of the substances involved, it is difficult to see how this claim can be denied or why anyone should wish to deny it. But there is no ground for the conclusion that the recent results obtained by physical methods invalidate any part of the classic theory of stereo-chemistry.

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[33] Weissenberg: Ber., 59, 1526 (1926); Henri: Chem. Reviews., 4, 189 (1927).

IX. Notes

A.

In certain cases (and particularly among unsaturated aliphatic compounds), where there are only two diameric stereoisomers, it is customary to refer to the relation between these compounds as one of "geometrical isomerism," and to call the two substances respectively the "cis" and "trans" forms. In other cases, where there are three stereo-isomers of which two are enantiomorphs, the third is commonly called the "meso" form. Among ring compounds, the distinction between these two varieties of diamerism breaks down. The optically inactive, unresolvable hexahydro-phthalic acid may be called either the cis or the meso form. And when more complex sets of stereo-isomers (such as the truxillic acids) are considered, the unqualified terms meso, cis and trans cease to have any unique significance. On account of the limited applicability of this terminology, it will not be used in the present article, which aims at a treatment as general as circumstances will permit. Any two stereo-isomers must be either diameric or enantiomorphous. Whether or not they happen to fall within the limited classes to which the above mentioned names apply is a matter which will here be disregarded.

B.

There is one small but important class of exceptions to the rule that the number of enantiomorphous pairs in $S_V(p)$ is a type property. Among certain restricted varieties of diphenyl derivatives, this number appears to depend on the specific nature of the univalent substituents. The most widely accepted theory on this subject is that of Mills.[34] If his reasoning is followed, it is to be predicted that octabromo-diphenic acid should exist in enantiomorphous forms but that diphenic acid should not. If the skeleton chosen in both of these cases be the united carbon rings of the diphenyl molecule, then d is 10 and (p) is (8,2). As the distribution of the 8 and 2 univalent substituents is also the same in each case, it is obvious that the difference in the number of enantiomorphous pairs must be due to specific differences in the univalent substituents themselves.

Since the revolutionary nature of Mills' theory has not been sufficiently recognized, it is hoped to treat these remarkable compounds in greater detail later on. For the present, it is enough to point out that in this small class of cases, the symbol $N_V(p)$ has no definite meaning. In these instances, a knowledge of V and (p) is not sufficient to permit the calculation of the number of isomers. The additional item necessary is probably the number of hydrogen atoms among the univalent substituents. Consequently such compounds are explicitly ruled out from all that follows in regard to the value of $N_V(p)$.

The class of compounds in which the number of univalent substitution isomers ceases to be a type property has been extended beyond the limits

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[34] Mills: Chemistry and Industry, 45, 884, 905 (1926). Cf. also Meisenheimer and Höring: Ber., 60, 1425 (1927); Mascarelli: Atti. Accad. Lincei, (6), 6, 60 (1927).

of the diphenyl derivatives.[35] Probably the number of instances of this sort of "specific enantiomorphism" is destined to increase considerably. Nevertheless, for the present at least, the whole class forms only a small exception to the general rule that the value of $N_V(p)$ is independent of the specific nature of the univalent substituents. And it is further to be noted that even in these cases, $N'_V(p)$ and $N''_V(p)$ are true type properties.

C.

From this point on, it is necessary to assume on the part of the reader an understanding of the elementary portion of the theory of groups, as well as an acquaintance with the terminology used by workers in this field. All that is necessary in this line may be obtained from any standard work on group theory.[36]

To use the formulae herein developed, it is necessary to have access to the lists of permutation groups of given degree. Easton in his bibliography gives a resumé of the literature in this field.[37] All the permutation groups of degree less than 12 have been determined, and all the transitive permutation groups of degree less than 16 likewise. The lists of groups are given in the notation devised by Cayley and explained by him in the first paper cited.[38] The articles noted contain all that is needful for a working knowledge of the subject.

But, for the purposes of the present paper, the number of permutation groups of degree n ($n < 12$) cannot be taken just as Easton gives it. A group given as of degree n must also be considered as a group of degree $n + x$ where x is any positive integer. Hence the following table:

Degree	Number of groups (as given by Easton)	Number of groups (here considered)	Degree	Number of groups (as given by Easton)	Number of groups (here considered)
1	1	1	7	40	96
2	1	2	8	200	296
3	2	4	9	258	554
4	7	11	10	1039	1593
5	8	19	11	1500	3093
6	37	56			

A simple extension of the Cayley notation serves to identify the additional groups thus introduced. The symbol $(abcd)_8(c)(f)$ indicates the group $(abcd)_8$, usually thought of as of degree 4, but here considered as of degree 6; the symbol [(*abcd*)all(*ef*)]dim(*g*) indicates the group [(*abcd*)all(*ef*)]dim, usually thought of as of degree 6, but here considered as of degree 7; etc., etc. In this sense, the identity group on five letters (for example) is (*a*)(*b*)(*c*)(*d*)(*e*). Such symbols are used in Table II.

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[35] Mills: J. Chem. Soc., **1928**, 1291; Kuhn and Albrecht: Ann., **464**, 91; **465**, 282 (1928).

[36] See e.g. Miller, Blichfeldt and Dickson: "Theory and Applications of Finite Groups" (1916).

[37] Easton: "The Constructive Development of Group Theory," pp. 77, 78 (1902).

[38] Cayley: Quart. Math., **25**, 71, 137; Cole: **26**, 372; **27**, 39; Miller: **27**, 99; **28**, 193; **29**, 224; **32**, 342; Am. J. Math. **21**, 287; Proc. London Math. Soc., **28**, 533; Bull. Am. Math. Soc., **1**, 67; Kuhn: **6**, 260.

D.

The formulae developed by Kauffmann[39] for the number of univalent substitution derivatives of quinoline, quinoxaline and naphthalene are all special cases of formula (B). The groups are as follows:

Molecule	Group
Quinoline	*(a)(b)(c)(d)(e)(f)(g)*
Quinoxaline	*(ab.cd.ef)*
Naphthalene	$(abcd.efgh)_4$

All of these groups are multiregular.

The group of naphthalene will be considered in more detail as an example. It consists of the four following operations:

1
ab.cd.ef.gh
ac.bd.eg.fh
ad.bc.eh.fg

The value of d is 8 and that of g is 4. In the equation

$$Z_G(d_f,\ d_2, \ldots, d_f) = \frac{1}{g}\sum_c \frac{n_c\left(\frac{d}{c}\right)!}{\left(\frac{d_1}{c}\right)!\left(\frac{d_2}{c}\right)!\ldots\left(\frac{d_f}{c}\right)!}$$

c has successively the values of all the common factors of g and $d_1, d_2 \ldots d_f$. And since, in the case under consideration, g is 4, c can have only the values 1, 2 and 4. But

$n_1 = 1$
$n_2 = 3$
$n_4 = 0$

and so the term where c is 4 always vanishes. There is always a term where c is 1 and n_1 is 1 no matter what the values of $d_1, d_2 \ldots d_f$, but the term where c is 2 and n is 3 appears only where the set $d_1, d_2 \ldots d_f$ is composed entirely of even integers. Hence the formula for the number of naphthalene derivatives becomes

$$Z_G(d_1, d_2, \ldots d_f) = \frac{1}{4}\left(\frac{8!}{d_1!\, d_2! \ldots d_f!}\right) + \frac{3}{4}\left(\frac{\left(\frac{8}{2}\right)!}{\left(\frac{d_1}{2}\right)!\left(\frac{d_2}{2}\right)!\ldots\left(\frac{d_f}{2}\right)!}\right)$$

$$= \frac{1}{4}\left(\frac{8!}{d_1!\, d_2! \ldots d_f!} + \frac{3 \times 4!}{\left(\frac{d_1}{2}\right)!\left(\frac{d_2}{2}\right)!\ldots\left(\frac{d_f}{2}\right)!}\right)$$

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[39] Kauffman: Ber., 33, 2131 (1900); "Die Valenzlehre," pp. 127-130, (1911); "Neues Handwörterbuch der Chemie, 7, 564-567 (1905). See also Noelting; Mon. sci., (4) 8, 178, (1894); and Rey: Ber., 33, 1910 (1900).

it being understood that the second term is applied only where $d_1, d_2 \ldots . d_t$ are all even integers. This expression is essentially identical with Kauffmann's formula.

It is difficult to determine from Kauffmann's published work just how general a setting he had in mind for the formulae he used. Although he does not make explicit use of the group concept, he speaks of the "symmetry lines" of his diagrams and recognizes their importance in determining the constants of his formulae. But he does not say just how he arrives at these constants. There is, for example, no statement of how he got the constant 3 which appears in the second term of his formula for the number of naphthalene derivatives. The group analysis explains it by the fact that there are 3 operations of the second order in the group $(abcd.efgh)_4$.

Kauffmann[40] does make the definite statement that his formulae apply only to molecules where no hydrogen atom lies on any symmetry line of the diagram—which in his cases is the necessary and sufficient condition that the group of the skeleton be multiregular. He refers[41] to the case of benzene (where the group is not multiregular) as a more difficult problem, and states that in conjunction with Hell he arrived at a formula for the numbers of substitution derivatives of this substance also. But according to a private communication, this result has not yet been published.

In developing his formulae Kauffmann makes use of a function F(n) which is such that

(1) $F(n) = n!$ where n has any real, positive, integral value.
(2) $F(n) = \infty$ where n has any other value.

To this function he attaches great importance, and states (Berichte, p. 2134) that it will probably suffice for the solution of the problem of the number of isomers among paraffin derivatives. But in the opinion of the present authors, this function F(n) or any similar function is superfluous. In cases like the formula for the number of naphthalene derivatives, its use may be obviated merely by defining c as a common factor of g and $d_1, d_2 \ldots . d_t$. Among paraffin derivatives, similar simple definitions serve to accomplish the same purpose. The key to the problems which Kauffmann attacked is the theory of permutation groups, and the considerable success which attended his efforts is due to the fact that he used in effect certain principles of group theory, although apparently unconsciously. The F function which he introduced tends to obscure the essentially Diophantine nature of the problem; hence it seems better to avoid it.

If, however, it is desired to use such a function, the conditions (1) and (2) cited above serve as a sufficient definition. To define the function by the use of expressions containing continued products is an unnecessary complication. It may be possible to express the required F(n) in this way, but the development given by Kauffmann (Handwörterbuch, Hell and Häussermann: loc. cit.) is unintelligible because of the divergence of the infinite products used.

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[40] "Die Valenzlehre," p. 129 (1911).

[41] Ber., 33, 2134 (1900).

X. Tables

Table I —Values of K. The omitted values of K in the upper right hand half of each section of this table are all equal to zero. In each column of values for (t), the vacuous set of integers which represent the identity is indicated by a dash.

Table II —Values of $Z_G(p)$. In the section for degree five, the underlined number in each column is the last integer (counting from the top) necessary for the unique determination of G.

TABLE I - VALUES OF K

3	1		
2	1	1	
–	1	3	6
(t) / (p)	3	2 1	1 1 1

d=3

4	1				
3	1	1			
2, 2	1	0	2		
2	1	2	2	2	
–	1	4	6	12	24
(t) / (p)	4	3 1	2 2	2 1 1	1 1 1 1

d=4

5	1						
4	1	1					
3, 2	1	0	1				
3	1	2	1	2			
2, 2	1	1	2	0	2		
2	1	3	4	6	6	6	
–	1	5	10	20	30	60	120
(t) / (p)	5	4 1	3 2	3 1 1	2 2 1	2 1 1 1	1 1 1 1 1

d=5

TABLE I – VALUES OF K

(t) \ (p)	6	5, 1	4, 2	4, 1, 1	3, 3	3, 2, 1	3, 1, 1, 1	2, 2, 2	2, 2, 1, 1	2, 1, 1, 1, 1	1, 1, 1, 1, 1, 1
6	1										
5	1	1									
4, 2	1	0	1								
4	1	2	1	2							
3, 3	1	0	0	0	2						
3, 2	1	1	1	0	2	1					
3	1	3	3	6	2	3	6				
2, 2, 2	1	0	3	0	0	0	0	6			
2, 2	1	2	3	2	4	4	0	6	4		
2	1	4	7	12	8	16	24	18	24	24	
–	1	6	15	30	20	60	120	90	180	360	720

d=6

(t) \ (p)	7	6, 1	5, 2	5, 1, 1	4, 3	4, 2, 1	4, 1, 1, 1	3, 3, 1	3, 2, 2	3, 2, 1, 1	3, 1, 1, 1, 1	2, 2, 2, 1	2, 2, 1, 1, 1	2, 1, 1, 1, 1, 1	1, 1, 1, 1, 1, 1, 1
7	1														
6	1	1													
5, 2	1	0	1												
5	1	2	1	2											
4, 3	1	0	0	0	1										
4, 2	1	1	1	0	1	1									
4	1	3	3	6	1	3	6								
3, 3	1	1	0	0	2	0	0	2							
3, 2, 2	1	0	2	0	1	0	0	0	2						
3, 2	1	2	2	2	3	2	0	4	2	2					
3	1	4	6	12	5	12	24	8	6	12	24				
2, 2, 2	1	1	3	0	3	3	0	0	6	0	0	6			
2, 2	1	3	5	6	7	9	6	12	14	12	0	18	12		
2	1	5	11	20	15	35	60	40	50	80	120	90	120	120	
–	1	7	21	42	35	105	210	140	210	420	840	630	1,260	2,520	5,040

d=7

TABLE I - VALUES OF K

8	1																					
7	1	1																				
6, 2	1	0	1																			
6	1	2	1	2																		
5, 3	1	0	0	0	1																	
5, 2	1	1	1	0	1	1																
5	1	3	3	6	1	3	6															
4, 4	1	0	0	0	0	0	0	2														
4, 3	1	1	0	0	1	0	0	2	1													
4, 2, 2	1	0	2	0	0	0	0	2	0	2												
4, 2	1	2	2	2	2	2	0	2	2	2	2											
4	1	4	6	12	4	12	24	2	4	6	12	24										
3, 3, 2	1	0	1	0	2	0	0	0	0	0	0	0	2									
3, 3	1	2	1	2	2	0	0	4	4	0	0	0	2	4								
3, 2, 2	1	1	2	0	3	2	0	2	1	2	0	0	4	0	2							
3, 2	1	3	4	6	5	6	6	6	9	6	6	0	8	12	6	6						
3	1	5	10	20	11	30	60	10	25	30	60	120	20	40	30	60	20					
2, 2, 2, 2	1	0	4	0	0	0	0	6	0	12	0	0	0	0	0	0	0	24				
2, 2, 2	1	2	4	2	6	6	0	6	6	12	6	0	12	0	12	0	0	24	12			
2, 2	1	4	8	12	12	20	24	14	28	32	36	24	40	48	56	48	0	72	72	48		
2	1	6	16	30	26	66	120	30	90	120	210	360	140	210	300	480	720	360	540	720	720	
–	1	8	28	56	56	168	336	70	280	420	840	1,680	560	1,120	1,680	3,360	6,720	2,520	5,040	10,080	20,160	40,320
(t) (p)	8	7, 1	6, 2	6, 1, 1	5, 3	5, 2, 1	5, 1, 1, 1	4, 4	4, 3, 1	4, 2, 2	4, 2, 1, 1	4, 1, 1, 1, 1	3, 3, 2	3, 3, 1, 1	3, 2, 2, 1	3, 2, 1, 1, 1	3, 1, 1, 1, 1, 1	2, 2, 2, 2	2, 2, 2, 1, 1	2, 2, 1, 1, 1, 1	2, 1, 1, 1, 1, 1, 1	1, 1, 1, 1, 1, 1, 1, 1

d = 8

TABLE I - VALUES OF K

(t) / (p)	9	8 1	7 2	7 1 1	6 3	6 2 1	6 1 1 1	5 4	5 3 1	5 2 2	5 2 1 1	5 1 1 1 1	4 4 1	4 3 2	4 3 1 1	4 2 2 1	4 2 1 1 1	4 1 1 1 1 1	3 3 3	3 3 2 1	3 3 1 1 1	3 2 2 2	3 2 2 1 1	3 2 1 1 1 1	3 1 1 1 1 1 1	2 2 2 2 1	2 2 2 1 1 1	2 2 1 1 1 1 1	2 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1
9	1																													
8	1	1																												
7, 2	1	0	1																											
7	1	2	1	2																										
6, 3	1	0	0	0	1																									
6, 2	1	1	1	0	1	1																								
6	1	3	3	6	1	3	6																							
5, 4	1	0	0	0	0	0	0	1																						
5, 3	1	1	0	0	1	0	0	1	1																					
5, 2, 2	1	0	2	0	0	0	0	1	0	2																				
5, 2	1	2	2	2	2	2	0	1	2	2	2																			
5	1	4	6	12	4	12	24	1	4	6	12	24																		
4, 4	1	1	0	0	0	0	0	2	0	0	0	0	2																	
4, 3, 2	1	0	1	0	1	0	0	1	0	0	0	0	0	1																
4, 3	1	2	1	2	1	3	0	3	2	0	0	0	4	1	2															
4, 2, 2	1	1	2	0	2	2	0	2	0	2	0	0	2	2	0	2														
4, 2	1	3	4	6	4	6	6	4	6	6	6	0	6	4	6	6	6													
4	1	5	10	20	10	30	60	6	20	30	60	120	10	10	20	30	60	120												
3, 3, 3	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	6											
3, 3, 2	1	1	1	0	3	1	0	2	2	0	0	0	0	2	0	0	0	0	6	2										
3, 3	1	3	3	6	3	3	6	6	6	0	0	0	12	6	12	0	0	0	6	6	12									
3, 2, 2, 2	1	0	3	0	1	0	0	3	0	6	0	0	0	3	0	0	0	0	0	0	0	6								
3, 2, 2	1	2	3	2	0	4	0	3	6	6	4	0	4	7	2	4	0	0	12	8	0	6	4							
3, 2	1	4	7	12	9	16	24	11	20	18	24	24	24	23	36	24	24	0	24	32	48	18	24	24						
3	1	6	15	30	21	60	120	21	66	20	180	360	60	75	150	180	960	720	60	120	240	90	180	360	720					
2, 2, 2, 2	1	1	4	0	4	4	0	6	0	12	0	0	6	12	0	12	0	0	0	0	0	24	0	0	0	24				
2, 2, 2	1	3	6	6	10	12	6	12	18	24	18	0	18	30	18	36	18	0	36	36	0	60	36	0	0	72	36			
2, 2	1	5	12	20	20	40	60	26	60	72	100	120	70	100	140	180	180	120	120	200	240	240	280	240	0	360	360	240		
2	1	7	22	42	42	112	210	56	182	252	672	840	210	350	630	840	1,470	2,520	420	980	1,680	1,260	2,100	3,360	5,040	2,520	3,780	5,040	5,040	
–	1	9	36	72	84	252	504	126	504	756	1,512	3,024	630	1,260	2,520	3,780	7,560	15,120	1,680	5,040	10,080	7,560	15,120	30,240	60,480	22,680	45,360	90,720	181,440	362,880

d=9

TABLE I - VALUES OF K

(t) \ (p)	10	9, 1	8, 2	8, 1, 1	7, 3	7, 2, 1	7, 1, 1, 1	6, 4	6, 3, 1	6, 2, 2	6, 2, 1, 1	6, 1, 1, 1, 1	5, 5	5, 4, 1	5, 3, 2	5, 3, 1, 1	5, 2, 2, 1	5, 2, 1, 1, 1	5, 1, 1, 1, 1, 1
10	1																		
9	1	1																	
8, 2	1	0	1																
8	1	2	1	2															
7, 3	1	0	0	0	1														
7, 2	1	1	1	0	1	1													
7	1	3	3	6	1	3	6												
6, 4	1	0	0	0	0	0	0	1											
6, 3	1	1	0	0	1	0	0	1	1										
6, 2, 2	1	0	2	0	0	0	0	1	0	2									
6, 2	1	2	2	2	2	2	0	1	2	2	2								
6	1	4	6	12	4	12	24	1	4	6	12	24							
5, 5	1	0	0	0	0	0	0	0	0	0	0	0	2						
5, 4	1	1	0	0	0	0	0	1	0	0	0	0	2	1					
5, 3, 2	1	0	1	0	1	0	0	0	0	0	0	0	2	0	1				
5, 3	1	2	1	2	1	0	0	2	2	0	0	0	2	2	1	2			
5, 2, 2	1	1	2	0	2	2	0	1	0	2	0	0	2	1	2	0	2		
5, 2	1	3	4	6	4	6	6	3	6	6	6	0	2	3	4	6	6	6	
5	1	5	10	20	10	30	60	5	20	30	60	120	2	5	10	20	30	60	120
4, 4, 2	1	0	1	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0
4, 4.	1	2	1	2	0	0	0	2	0	0	0	0	4	4	0	0	0	0	0
4, 3, 3	1	0	0	0	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0
4, 3, 2	1	1	1	0	2	1	0	2	1	0	0	0	2	1	1	0	0	0	0
4, 3	1	3	3	6	2	3	6	4	3	0	0	0	6	9	3	6	0	0	0
4, 2, 2, 2	1	0	3	0	0	0	0	4	0	6	0	0	0	0	0	0	0	0	0
4, 2, 2	1	2	3	2	4	4	0	4	4	6	4	0	4	4	4	0	4	0	0
4, 2	1	4	7	12	8	16	24	8	16	18	24	24	8	16	16	24	24	24	0
4	1	6	15	30	20	60	120	16	60	90	180	360	12	36	60	120	180	360	720
3, 3, 3	1	1	0	0	3	0	0	3	3	0	0	0	0	0	0	0	0	0	0
3, 3, 2, 2	1	0	2	0	2	0	0	1	0	2	0	0	4	0	4	0	0	0	0
3, 3, 2	1	2	2	2	4	2	0	5	6	2	2	0	4	4	4	4	0	0	0
3, 3	1	4	6	12	6	12	24	9	12	6	12	24	12	24	12	24	0	0	0
3, 2, 2, 2	1	1	3	0	4	3	0	4	1	6	0	0	6	3	9	0	6	0	0
3, 2, 2	1	3	5	6	8	9	6	10	15	14	12	0	4	15	19	18	18	12	0
3, 2	1	5	11	20	16	35	60	20	45	50	80	120	22	55	61	100	90	120	120
3	1	7	21	42	36	105	210	42	147	210	420	840	42	147	231	462	630	1260	2520
2, 2, 2, 2, 2	1	0	5	0	0	0	0	10	0	20	0	0	0	0	0	0	0	0	0
2, 2, 2, 2	1	2	5	2	8	8	0	10	8	20	8	0	12	12	24	0	24	0	0
2, 2, 2	1	4	9	12	16	24	24	22	40	48	48	24	24	48	72	72	96	72	0
2, 2	1	6	17	30	32	72	120	46	120	152	240	360	52	156	232	360	432	600	720
2	1	8	28	56	64	176	336	98	336	476	896	1680	112	448	794	1456	2016	3696	6720
-	1	10	45	90	120	360	720	210	840	1260	2520	5040	252	1260	2520	5040	7560	15120	30240

d=10

TABLE I - VALUES OF K

(t) / (p)	4,4,2	4,4,1,1	4,3,3	4,3,2,1	4,3,1,1,1	4,2,2,2	4,2,2,1,1	4,2,1,1,1,1	4,1,1,1,1,1,1	3,3,3,1	3,3,2,2	3,3,2,1,1	3,3,1,1,1,1	3,2,2,2,1	3,2,2,1,1,1	3,2,1,1,1,1,1	3,1,1,1,1,1,1,1	2,2,2,2,2	2,2,2,2,1,1	2,2,2,1,1,1,1	2,2,1,1,1,1,1,1	2,1,1,1,1,1,1,1,1	1,1,1,1,1,1,1,1,1,1
4, 4, 2	2																						
4, 4	2	4																					
4, 3, 3	0	0	2																				
4, 3, 2	2	0	2	1																			
4, 3	6	12	2	3	6																		
4, 2, 2, 2	6	0	0	0	0	6																	
4, 2, 2	6	4	4	4	0	6	4																
4, 2	14	24	8	16	24	18	24	24															
4	30	60	20	60	120	90	180	360	720														
3, 3, 3	0	0	6	0	0	0	0	0	0	6													
3, 3, 2, 2	0	0	2	0	0	0	0	0	0	0	4												
3, 3, 2	4	0	10	4	0	0	0	0	0	12	4	4											
3, 3	24	48	18	24	48	0	0	0	0	24	12	24	48										
3, 2, 2, 2	6	0	6	3	0	6	0	0	0	0	12	0	0	6									
3, 2, 2	18	12	26	18	6	18	12	0	0	36	28	24	0	18	12								
3, 2	70	120	70	115	180	90	120	120	0	120	100	160	240	90	120	120							
3	210	420	210	525	1,050	630	1,260	2,520	2,040	420	420	840	1,680	630	1,260	2,520	5,040						
2, 2, 2, 2, 2	30	0	0	0	0	60	0	0	0	0	0	0	0	0	0	0	0	120					
2, 2, 2, 2	30	12	24	24	0	60	24	0	0	0	48	0	0	48	0	0	0	120	48				
2, 2, 2	72	72	96	120	72	168	144	72	0	144	192	144	0	240	144	0	0	360	288	144			
2, 2	270	420	300	600	840	720	960	1,080	720	720	880	1,200	1,440	1,440	1,680	1,440	0	1,800	2,160	4,160	1,440		
2	910	1,680	1,120	2,800	5,040	3,780	6,720	11,760	20,160	3,360	4,480	7,840	13,440	10,080	16,800	26,880	40,320	12,600	20,160	30,240	40,320	40,320	
	3,150	6,300	4,200	12,600	25,200	18,900	37,800	75,600	151,200	16,800	25,200	50,400	100,800	75,600	151,200	302,400	604,800	113,400	226,800	453,600	907,200	1,814,400	3,628,800

d=10 (cont'd)

TABLE II - VALUES OF $Z_G(p)$

Order	1	2	3	6
G / (p)	(a)(b)(c)	(ab)(c)	(abc) cyc	(abc) all
3	1	1	1	1
2, 1	3	2	1	1
1, 1, 1	6	3	2	1

d=3

Order	1	2	2	3	4	4	4	6	8	12	24
G / (p)	(a)(b)(c)(d)	(ab)(c)(d)	(ac.bd)	(abc) cyc (d)	(ac)(bd)	$(abcd)_4$	(abcd) cyc	(abc) all (d)	$(abcd)_8$	(abcd) pos	(abcd) all
4	1	1	1	1	1	1	1	1	1	1	1
3, 1	4	3	2	2	2	1	1	2	1	1	1
2, 2	6	4	4	2	3	3	2	2	2	1	1
2, 1, 1	12	7	6	4	4	3	3	3	2	1	1
1, 1, 1, 1	24	12	12	8	6	6	6	4	3	2	1

d=4

TABLE II - VALUES OF $Z_G(p)$

Order	1	2	2	3	4	4	4	5	6	6	6	8	10	12	12	20	24	60	120
(p) \ G	(a)(b)(c)(d)(e)	(ab)(c)(d)(e)	(ac.bd)(e)	(abc) cyc (d)(e)	(ac)(bd)(e)	$(abcd)_4$ (e)	(abcd) cyc (e)	(abcde) cyc	(abc) all (d)(e)	(abc) cyc (de)	{(abc) all (de)} pos	$(abcd)_8$ (e)	$(abcde)_{10}$	(abcd) pos (e)	(abc) all (de)	$(abcde)_{20}$	(abcd) all (e)	(abcde) pos	(abcde) all
5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
4,1	$\underline{5}$	$\underline{4}$	3	3	3	2	2	1	3	2	2	2	1	2	2	1	2	1	1
3,2	10	7	$\underline{6}$	4	$\underline{5}$	$\underline{4}$	3	2	4	3	3	3	2	2	3	1	2	1	1
3,1,1	20	13	10	$\underline{8}$	8	5	5	$\underline{4}$	$\underline{7}$	5	4	4	$\underline{2}$	3	4	1	3	1	1
2,2,1	30	18	16	10	11	9	$\underline{8}$	6	8	$\underline{6}$	6	6	4	3	$\underline{5}$	$\underline{2}$	3	1	1
2,1,1,1	60	33	30	20	18	15	15	12	13	11	$\underline{10}$	$\underline{9}$	6	$\underline{5}$	7	3	$\underline{4}$	1	1
1,1,1,1,1	120	60	60	40	30	30	30	24	20	20	20	15	12	10	10	6	5	$\underline{2}$	$\underline{1}$

d=5

The underlined figure in each column is the last integer (counting from the top) necessary for the unique determination of G.

TABLE II - VALUES OF $Z_G(p)$

Order	1	2	2	2	3	3	4	4	4	4	4	4	4	5	6	6	6	6	6	6
(p) \ G	(a)(b)(c)(d)(e)(f)	(ab)(c)(d)(e)(f)	(ac.bd)(e)(f)	(ac.bd.ef)	(abc) cyc (d)(e)(f)	(abc.def) cyc	(ac)(bd)(e)(f)	$(abcd)_4$ (e)(f)	(abcd) cyc (e)(f)	(ac.bd)(ef)	{(ac)(bd)(ef)} pos	{$(abcd)_4$ (ef)} dis	{(abcd) cyc (ef)} pos	(abcde) cyc (f)	(abc) all (d)(e)(f)	(abc) cyc (de)(f)	{(abc) all (de)} pos (f)	(abc.def) all	(abcdef) cyc	$(abcdef)_6$
6	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5, 1	6	5	4	3	4	2	4	3	3	3	3	2	2	2	4	3	3	2	1	1
4, 2	15	11	9	9	7	5	8	6	5	7	6	6	5	3	7	5	5	4	3	4
4, 1, 1	30	21	16	15	14	10	14	9	9	11	9	8	8	6	13	9	8	6	5	5
3, 3	20	14	12	10	8	8	10	8	6	8	8	6	6	4	8	6	6	6	4	4
3, 2, 1	60	38	32	30	22	20	24	18	16	20	18	16	16	12	19	14	13	12	10	10
3, 1, 1, 1	120	72	60	60	44	40	42	30	30	36	30	30	30	24	34	26	22	20	20	20
2, 2, 2	90	54	48	48	30	30	33	27	24	30	27	27	24	18	24	18	19	18	16	18
2, 2, 1, 1	180	102	92	90	60	60	58	48	46	52	48	46	46	36	42	34	37	32	30	30
2, 1, 1, 1, 1	360	192	180	180	120	120	102	90	90	96	90	90	90	72	72	64	60	60	60	60
1, 1, 1, 1, 1, 1	720	360	360	360	240	240	180	180	180	180	180	180	180	144	120	120	120	120	120	120

d=6

TABLE II - VALUES OF $Z_G(p)$

Order	8	8	8	8	8	8	8	9	10	12	12	12	12	16	18	18	18	20
G / (p)	$(abcd)_8(e)(f)$	$(ac)(bd)(ef)$	$(abcd)$ cyc (ef)	$(abcd)_8(ef)$	{$(abcd)_8$ com(ef)}dim	{$(abcd)_8$ cyc(ef)}dim	{$(abcd)_8$ pos(ef)}dim	(abc) cyc (def) cyc	$(abcde)_{10}(f)$	$(abcd)$ pos $(e)(f)$	(abc) all $(de)(f)$	$(abcdef)_{12}$	$(abcdef)_{12_2}$	$(abcd)_8(ef)$	(abc) all (def) cyc	{(abc) all (def) all}pos	$(abcdef)_{18}$	$(abcde)_{20}(f)$
6	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5, 1	3	3	2	2	2	2	2	2	2	3	3	1	1	2	2	2	1	2
4, 2	5	6	4	5	5	4	4	3	3	4	5	3	2	4	3	3	2	2
4, 1, 1	8	9	6	6	7	5	5	6	4	7	8	3	3	6	5	4	3	3
3, 3	6	7	4	5	5	4	5	4	4	4	6	3	4	4	4	4	2	2
3, 2, 1	13	15	10	11	12	9	10	8	8	8	12	6	6	8	7	6	4	4
3, 1, 1, 1	21	24	18	18	21	15	15	16	12	14	19	10	10	12	12	8	8	6
2, 2, 2	18	21	15	18	18	15	15	10	12	9	15	11	9	12	8	8	6	6
2, 2, 1, 1	30	33	26	27	29	24	25	20	20	16	24	16	16	17	14	12	10	10
2, 1, 1, 1, 1	51	54	48	48	51	45	45	40	36	30	38	30	30	27	24	20	20	18
1, 1, 1, 1, 1, 1	90	90	90	90	90	90	90	80	72	60	60	60	60	45	40	40	40	36

d=6 (CONT'D)

TABLE II - VALUES OF $Z_G(p)$

Order	24	24	24	24	24	24	36	36	36	48	48	60	60	72	120	120	360	720
G / (p)	$(abcd)$ all $(e)(f)$	$(abcd)$ pos (ef)	{$(abcd)$ all (ef)}pos	$(\pm abcdef)_{24}$	$(+abcdef)_{24}$	$(abcdef)_{24_5}$	(abc) all (def) all	$(abcdef)_{36}$	$(abcdef)_{36_3}$	$(abcd)$ all (ef)	$(abcdef)_{48}$	$(abcde)$ pos (f)	$(abcdef)_{60}$	$(abcdef)_{72}$	$(abcde)$ all (f)	$(abcdef)_{120}$	$(abcdef)$ pos	$(abcdef)$ all
6	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5, 1	3	2	2	1	1	1	2	1	1	2	1	2	1	1	2	1	1	1
4, 2	4	3	3	2	2	2	3	2	2	3	2	2	1	2	2	1	1	1
4, 1, 1	7	4	4	2	2	3	4	2	2	4	2	3	1	2	3	1	1	1
3, 3	4	3	3	2	3	3	4	2	2	3	2	2	2	2	2	1	1	1
3, 2, 1	8	5	5	3	4	5	6	3	3	5	3	3	2	3	3	1	1	1
3, 1, 1, 1	13	8	7	5	5	8	8	4	4	7	4	4	2	4	4	1	1	1
2, 2, 2	9	6	6	6	6	7	7	4	5	6	5	3	3	4	3	2	1	1
2, 2, 1, 1	14	9	9	8	9	11	10	6	6	8	6	4	4	5	4	2	1	1
2, 1, 1, 1, 1	21	16	15	15	15	18	14	10	10	11	9	6	6	7	5	3	1	1
1, 1, 1, 1, 1, 1	30	30	30	30	30	30	20	20	20	15	15	12	12	10	6	6	2	1

d=6 (CONT'D)

GERMANIUM XXXI. ALLOYS OF GERMANIUM: SILVER-GERMANIUM

BY T. R. BRIGGS, R. O. McDUFFIE AND L. H. WILLISFORD

Part I. Introduction

When this investigation was begun in 1925, no alloy containing germanium had yet been studied in detail. Since that time, however, Kroll[1] has contributed an investigation of the system aluminum-germanium, and has been able to construct the phase diagram for mixtures containing up to 60 per cent of germanium. The diagram indicates that the two metals form a simple eutectiferous series of alloys in which the solid phases are the individual components.

In a second paper Kroll[2] goes on to show that germanium may replace silicon in alloys such as duralumin, aludur, and lautal, with marked improvement in their engineering properties. This discovery is interesting as suggesting a possible technical use for germanium in small quantities.

Silver was chosen as the second component because the system silver-germanium was thought likely to prove a simple one,[3] and also because it was possible that germanium might improve the resistance of silver to tarnish through the formation of a protective film of oxide. Accordingly, some of the alloys prepared in the course of this investigation were turned over to the United States Bureau of Standards, with the coöperation of Dr. H. W. Gillett, and their resistance to tarnish measured. The results of this special investigation have already been published.[4]

Part II. Thermal and Metallographic Examination of the Alloys

Preparation of the Metallic Germanium.

The metallic germanium was prepared in accordance with the method of Dennis, Tressler, and Hance,[5] by reducing the dioxide with hydrogen and fusing the finely divided metal under sodium chloride to bring about coalescence. Since the metal thus obtained melted at 925°—the accepted melting point of germanium being 958°—it was considered to be contaminated with

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[1] Metall und Erz., **23**, 682 (1926).

[2] Metall und Erz, **23**, 684 (1926).

[3] The system silver-silicon consists of a simple eutectiferous series containing silver and a silicon-rich solid solution as the solid phases. Cf. Arrivaut: Compt. rend., **147**, 859 (1908). The silver-tin alloys are more complex and comprise several solid solutions and possibly the compound Ag_3Sn. Cf. Murphy: J. Inst. Met., **35**, 187 (1926).

[4] Jordan, Grenall, and Herschman: Technologic Paper U. S. Bur. of Standards, No. 348 (1927).

[5] J. Am. Chem. Soc., **45**, 2033 (1923). The hydrogen was carefully purified in accordance with the method recommended by these authors and pure sodium chloride was likewise obtained by precipitation with hydrochloric acid and subsequent recrystallization.

dissolved oxide[1] and it was accordingly submitted to the special treatment recommended by Dennis and his coworkers for the removal of dissolved oxide.

This treatment consists in repeatedly melting and freezing the germanium in an atmosphere of purified hydrogen. After 42 meltings and freezings the melting point, as determined in the apparatus used in this work, rose to 943°, after which 90 more fusions brought it to 949°. Further treatment did not change the melting point, and as a spectrographic examination[2] failed to detect any appreciable quantities of impurities in the metal, it was decided to use the germanium thus prepared in the study of the alloys.

Preparation of the Alloys.

The silver was obtained from the Philadelphia Mint and no appreciable quantities of impurities were detected by spectrographic examination. The first alloy was made by adding the desired amount of silver to the whole of the available germanium (about 22 grams), and the alloy was then submitted to thermal analysis. When this was completed, part of the alloy was reserved for chemical analysis, optical examination, determination of electrical conductance, and so forth, and the residue was used to prepare the second alloy in the series by the addition of more silver. In view of this procedure, necessitated by the limited supply of germanium, it was not practicable to return to an alloy less rich in silver when carrying out the thermal examination of the whole series.

Thermal Analysis of the Alloys.

The alloys were prepared and subjected to thermal analysis in specially designed furnace and crucibles.[3] The metal in the crucible was protected against oxidation by means of a steady stream of purified hydrogen which was led through the cover of the crucible in a quartz delivery tube. As an additional precaution, the metal in the crucible was covered with a layer of specially prepared and purified sugar carbon, and a second layer of carbon was placed over the cover of the crucible itself, this outer layer being protected with a stream of nitrogen.

The matched Chromel-Alumel base-metal thermocouples were calibrated[4] carefully in the usual way. Care was taken to employ exactly the same furnace equipment and procedure as that which was used in the work with the alloys, particularly as regards the amount of metal in the crucible. As cali-

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[1] Cf. Biltz: Z. anorg. Chem., **72**, 313 (1911).

[2] Carried out by Professor Papish in this Laboratory.

[3] The furnace consisted of an electrically heated alundum crucible contained in a crock packed with Sil-o-Cel. The crucibles were prepared from Acheson graphite electrodes and were specially treated with hydrochloric acid and water to remove impurities, being examined spectrographically before use. Each crucible was equipped with a specially designed, closely fitting graphite cover, containing openings for the introduction of hydrogen and for the protection tube of the thermocouple.

[4] The thermocouple indicator was a Leeds and Northrup portable thermocouple pyrometer with manual cold junction compensation. This instrument was checked against a Type K potentiometer before use. "Impervite" protection tubes were used because fused quartz tubes collapsed too easily.

brating substances, tin, bismuth, cadmium, lead, zinc, antimony, sodium chloride, and silver were employed and the calibration curve thus got was used in the subsequent work.

In the determination of the melting point of the germanium, and in the thermal analysis of the first three alloys, direct (time vs. temperature) heating and cooling curves were taken. Although the method proved fairly satisfactory for these alloys, it was thought best to use a more sensitive method with the subsequent alloys of the series. For this purpose, accordingly, a sensitive galvanometer with lamp and scale was connected in parallel with the galvanometer of the potentiometer which was used with the thermocouple. During the cooling of the alloy, the potentiometer was set so as to displace the indicator (a beam of light) 15 or 20 divisions from the center of the scale on the second galvanometer, and the time required for the beam to pass through each five divisions of the scale was recorded. After the beam had passed the center and had reached 15 or 20 divisions on the opposite side, the potentiometer was re-set and the procedure repeated. As it was found that a swing through 5 divisions of the scale was equivalent to a change of 4.0 degrees in temperature, the data necessary for a differential cooling (or heating) curve were thus obtained.[1]

Sampling and Analysis of the Alloys.

Since germanium has a much smaller density than silver and so tends to float to the top of a melt from which it is solidifying, it becomes badly segregated[2] in a cast bar. Sampling the solid alloys for chemical analysis therefore proved difficult. Alloys rich in germanium were too brittle to drill properly, and when an attempt was made to crush the alloy, the germanium was reduced to a fine powder, while the silver in the eutectic was flattened into plates.

These difficulties in sampling, however, were overcome by removing small samples for analysis from the *molten* alloy. For this purpose a special sampling crucible was devised for use with a special graphite rod equipped with small, cup-like depressions for dipping up and retaining samples of molten alloy about 0.3 gram in weight,[3] each of which samples could be used

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[1] Care was taken to stir the metal thoroughly during each run; this was accomplished by manipulating the protection tube of the thermocouple as a stirring rod. In every case the thermal arrests found on cooling were confirmed by determining heating curves, and the work was repeated with progressively diminishing rates of cooling and heating, until the same temperatures were got by the two modes of procedure.

[2] Cf. Photomicrograph 11. This is a cast bar containing 62 atomic percent of germanium. Primary germanium crystals are segregated at the top in a matrix of nearly pure eutectic.

[3] The sampling crucible was made from a three-inch section of 1.5 inch graphite electrode, into which a cylindrical depression one inch in diameter and one inch deep was drilled. At the bottom of this depression and slightly off-center, a second hole 1.5 inches deep and 3/8 inch in diameter was drilled. The cover of this crucible was like the one used with the crucibles which were employed in the thermal analysis, except that it was fitted with an extra opening to permit the introduction of the sampling rod. The latter consisted of a short section of 3/8 inch graphite rod to which was fitted a glass handle, and into which near the lower end were drilled two small cup-like depressions, slanting downward in order to dip up and hold the desired amount of molten alloy.

in its entirety for a single chemical analysis. Care was taken to proceed[1] in such a way as to insure the sample being uniform, and to cool it in an atmosphere of hydrogen.

With the sampling rod, concordant chemical analyses were obtained. For example, duplicate analyses of Alloy 7 gave 48.0 and 48.15 atomic percent of

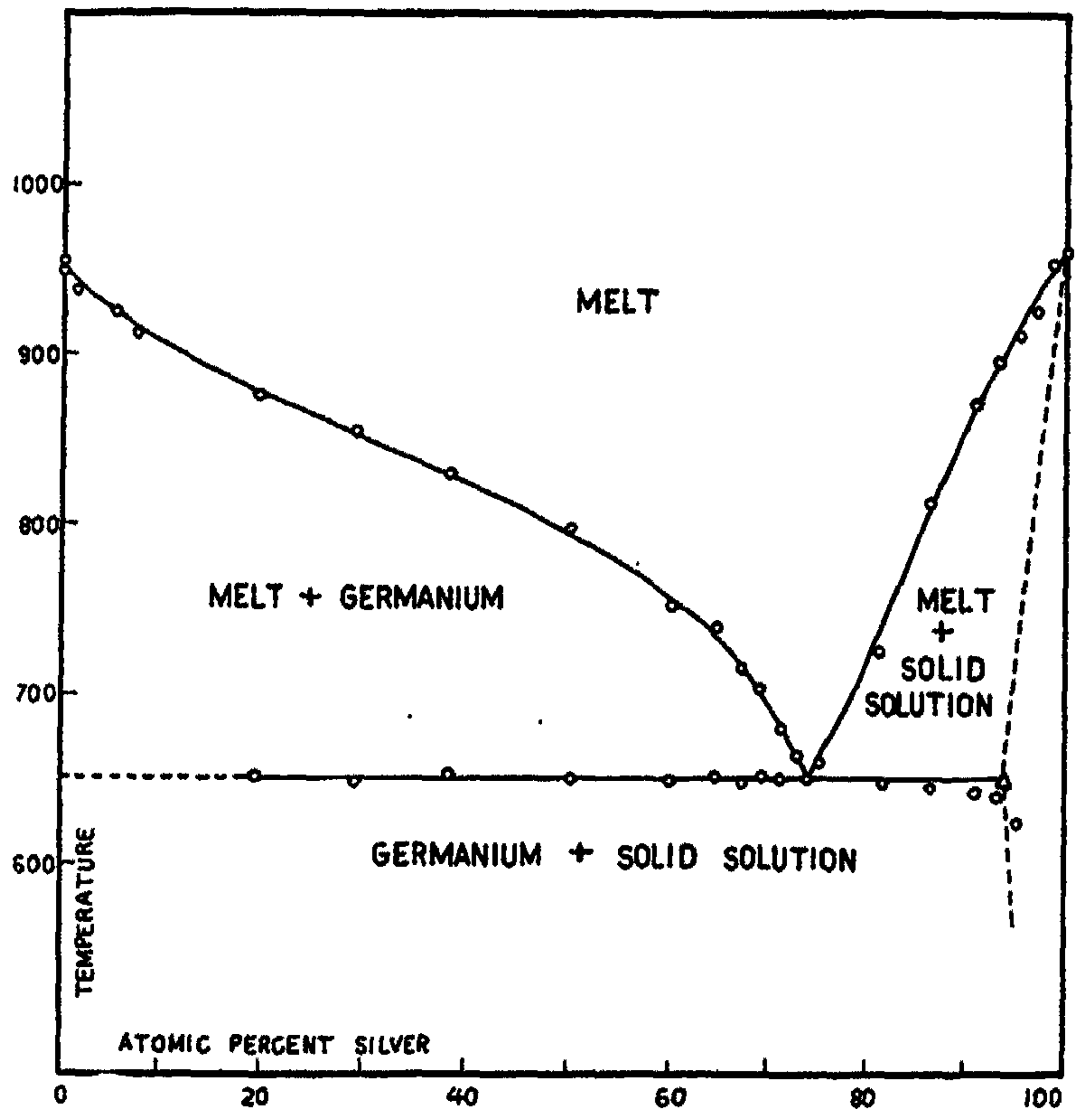

FIG. 1
Equilibrium Diagram

silver respectively, while with Alloy 6, sampled by crushing and quartering, the results were 36.9, 45.2, and 39.9, and were therefore far from satisfactory.

The silver in the dipped samples of each alloy was determined by Volhard's method, the germanium being found by difference. The alloy was

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[1] The alloy to be sampled was broken up and placed in the lower depression in the crucible, and the protection tube of the thermocouple, the delivery tube for the hydrogen, and the sampling rod were placed in position, the latter being directly over the narrow depression holding the alloy. The top of the crucible was covered with a protecting layer of sugar carbon. When the contents became liquid, the sampling rod was forced up and down in the lower depression to stir the alloy, and after ten minutes of this, it was raised carefully until the cups filled with alloy were suspended in the middle of the large upper chamber in the crucible, and the samples for analysis were allowed to cool out of contact with the rest of the metal in the crucible.

dissolved in a warm mixture of hydrogen peroxide (from perhydrol) and dilute nitric acid; this was then boiled to remove the oxides of nitrogen and the excess of peroxide, after which it was titrated with ammonium thiocyanate with ferric alum as indicator.

Metallographic Examination of the Alloys.

The thermal analysis of each alloy was supplemented by a careful microscopic examination of cast and annealed specimens. Either relief polishing or etching[1] was used, the former giving the best results with alloys rich in germanium, and the latter the best results with alloys rich in silver. The photomicrographs were taken with either a Leitz or a Bausch and Lomb metallograph, equipped with yellow filter and panchromatic plates.[2]

The Thermal Data.

The thermal data for the whole series of alloys are given in Table I, and they have been plotted on the equilibrium diagram, Fig. 1. In obtaining these data the temperature of each arrest was taken to be the point where the inverse-rate cooling curve first breaks away from the perpendicular.[3]

The thermal data indicate that the alloys of silver and germanium form a simple eutectiferous series. The single eutectic mixture melts at 650° and contains 74 atomic per cent of silver. The thermal data alone afford insufficient evidence to prove that the solid phases are pure germanium and pure silver—instead there may be one pure component and a saturated solid solution, or two conjugate solid solutions. These possibilities will be considered later. At any rate, there are apparently no stable intermetallic compounds.

It will be noticed that the second arrest for Alloys 18 to 20 inclusive falls considerably below the average of the other eutectic arrests (650°). This behavior is normal for alloys which are far removed from the composition of the eutectic, and it is due to the greatly increased lag in temperature between the molten eutectic and the thermocouple, this lag being caused by the phase which is in excess crystallizing out and coating the protection tube before the eutectic temperature is reached.

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[1] Pure germanium was etched 15 minutes in an aqueous solution containing 5 parts of hydrogen peroxide and 30 parts of concentrated hydrochloric acid. The silver alloys were etched, either by immersion in 1:5 solution of hydriodic acid until a film of silver iodide had formed (which was then dissolved off in concentrated potassium iodide), or by immersion in a fairly concentrated solution of potassium iodide containing hydriodic acid.

[2] Since the structure of many of the alloys was developed by relief polishing, the surface of the germanium crystals was at a slightly higher level than the eutectic which surrounded them. Yellow light was therefore employed to give greater depth of focus. Since most of the structures were fairly coarse, the loss of resolving power through the use of yellow light was of minor importance. Panchromatic plates were used so as to obtain the necessary sensitivity to yellow light.

[3] This is the logical method to use, since the first break in the cooling curve indicates an evolution of heat within the alloy, and this in turn can only be caused by a change of phase, or in other words by the alloy starting to freeze. The peak of the curve, which represents the minimum rate of cooling for the alloy, may come at a somewhat lower temperature than the freezing point, and will do so in a binary alloy not of eutectic composition, because the crystallization of one of the constituents changes the composition of the liquid phase, and thus lowers progressively the temperature of solidification. Even in the case of an eutectic arrest the peak may be at a lower temperature than the eutectic point if there is a difference in temperature between the alloy and the hot junction of the thermocouple.

TABLE I

Thermal Data

Alloy (Number)	Composition (Atomic per cent silver)	Temperature (°C) First Arrest	Second Arrest
(Germanium)	0.0	949	—
1	1.21	937	(Not determined)
2	5.50	925	(Not determined)
3	7.65	913	(Not determined)
4	19.7	876	651
5	29.2	855	649
6	38.2	830	652
7	50.3	797	650
8	60.2	753	649
9	64.3	740	653
10	67.2	715	649
11	69.2	705	652
12	71.4	680	650
13	73.0	665	651
14	74.0	650	650
15	75.3	660	651
16	81.4	725	647
17	87.1	812	646
18	91.2	870	642
19	93.2	896	640
20	95.3	912	625
21	96.9	925	None
22	98.5	953	None
(Silver)	100	961	—

On the other hand it is desirable to ascertain at what compositions the eutectic arrest disappears in a given series of alloys, for in this way one can determine whether solid solutions are formed and, if they are, within what limits of composition they lie. Since it is not easy to detect an eutectic arrest near the two extremes of the composition diagram, Tammann[1] has suggested plotting the duration of the eutectic arrest as a function of composition, and estimating by an extrapolation the composition at which the duration falls to zero. Success with the method demands the maintainance of constant conditions for every alloy, and as Desch[2] has pointed out, requires a comparatively large quantity of material. The last requirement precluded the application of Tammann's method to the present system, and no attempt was made to use it. Consequently, for information on the existence and limits of solid solutions of silver and germanium, it was necessary to rely entirely upon metallographic evidence.

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[1] Z. anorg. Chem., 37, 303 (1903); 45, 24 (1904); 47, 291 (1905).

[2] "Metallography," 309 (1922).

The melting point of germanium, as determined in this investigation, appears to be low (Cf. Table I). Biltz[1], working with small amounts of the metal, found the melting point to be 958° ± 5° in an atmosphere of hydrogen. Dennis, Tressler, and Hance[2] obtained 958.5°, in close agreement with Biltz. Likewise Müller, Pike, and Graham[3] reported 959° as the temperature at which germanium begins to flow in an atmosphere of hydrogen, which temperature they take as the melting point in hydrogen, the melting point in vacuo being said to be 975°. Of these three determinations, the only one made with a reasonably large mass of germanium in accordance with standard practice is the one reported by Dennis and his coworkers.

After the publication of the present investigation in the form of a thesis, a special re-determination of the melting point of germanium was carried out by Mr. F. H. Roninger as part of his work in Senior Research. A fresh sample of germanium, after being treated in hydrogen to remove oxide, was put into a purified graphite crucible and covered with pure powdered graphite, the whole being placed in a special quartz tube heated in an electric furnace. The quartz tube was closed at its lower end, and was long enough so that it extended some distance above the top of the furnace. The open upper end of this tube was fitted with a stopper containing the inlet for the hydrogen and the protection tube for the thermocouple, the latter having been previously calibrated against a standard thermocouple bearing a recent certificate from the Bureau of Standards. With this apparatus and equipment a very satisfactory cooling curve was obtained and the melting point was found to be 955° ± 2.5°.

Accordingly, in view of the findings of previous investigators, and the later work of Mr. Roninger, the melting point (949°) recorded in this communication is very probably slightly in error. It seems likely that the germanium became somewhat contaminated with oxide while the melting point was being determined. The error however does not seem great enough to affect seriously the equilibrium diagram.

Photomicrographic Analysis.

During the investigation photomicrographs of each alloy were obtained. Some of these accompany this article. Photomicrographs 1 to 8 inclusive suffice as a survey of the whole series, as follows:—

Photomicrograph 1 — Alloy 3, atomic per cent silver = 7.65
Photomicrograph 2 — Alloy 6, atomic per cent silver = 38.2
Photomicrograph 3 — Alloy 8, atomic per cent silver = 60.2
Photomicrograph 4 — Alloy 13, atomic per cent silver = 73.0
Photomicrograph 5 — Alloy 14, (eutectic), atomic per cent silver = 74.0
Photomicrograph 6 — Alloy 15, atomic per cent silver = 75.3
Photomicrograph 7 — Alloy 16, atomic per cent silver = 81.4
Photomicrograph 8 — Alloy 17, atomic per cent silver = 87.1

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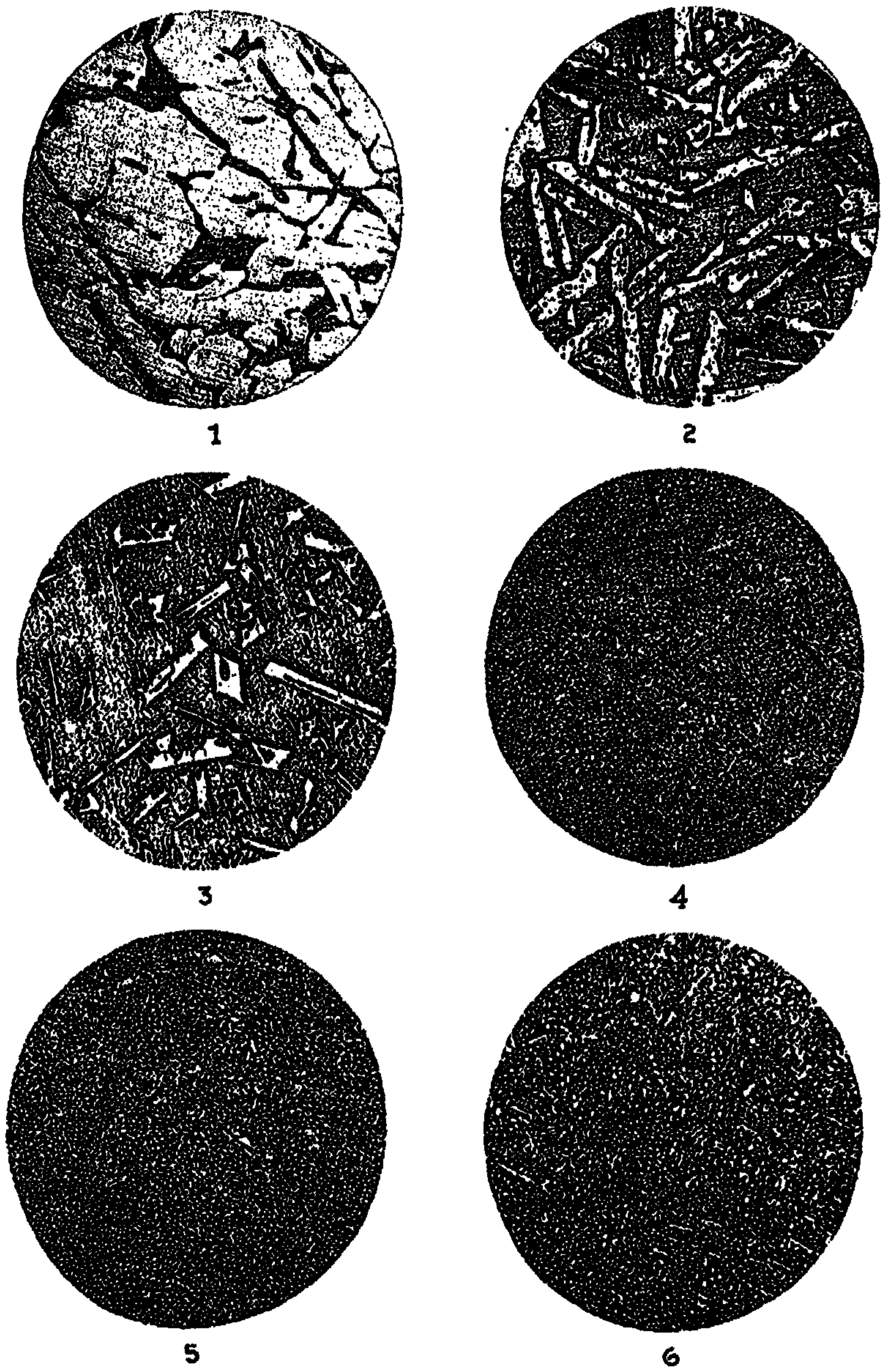
[1] Z. anorg. Chem., 72, 313 (1911).
[2] Loc. cit.: J. Am. Chem. Soc., 45, 2033 (1923).
[3] Proc. Am. Phil. Soc., 65, 15 (1926).



1 2

3 4

5 6

PLATE I. Photomicrographs

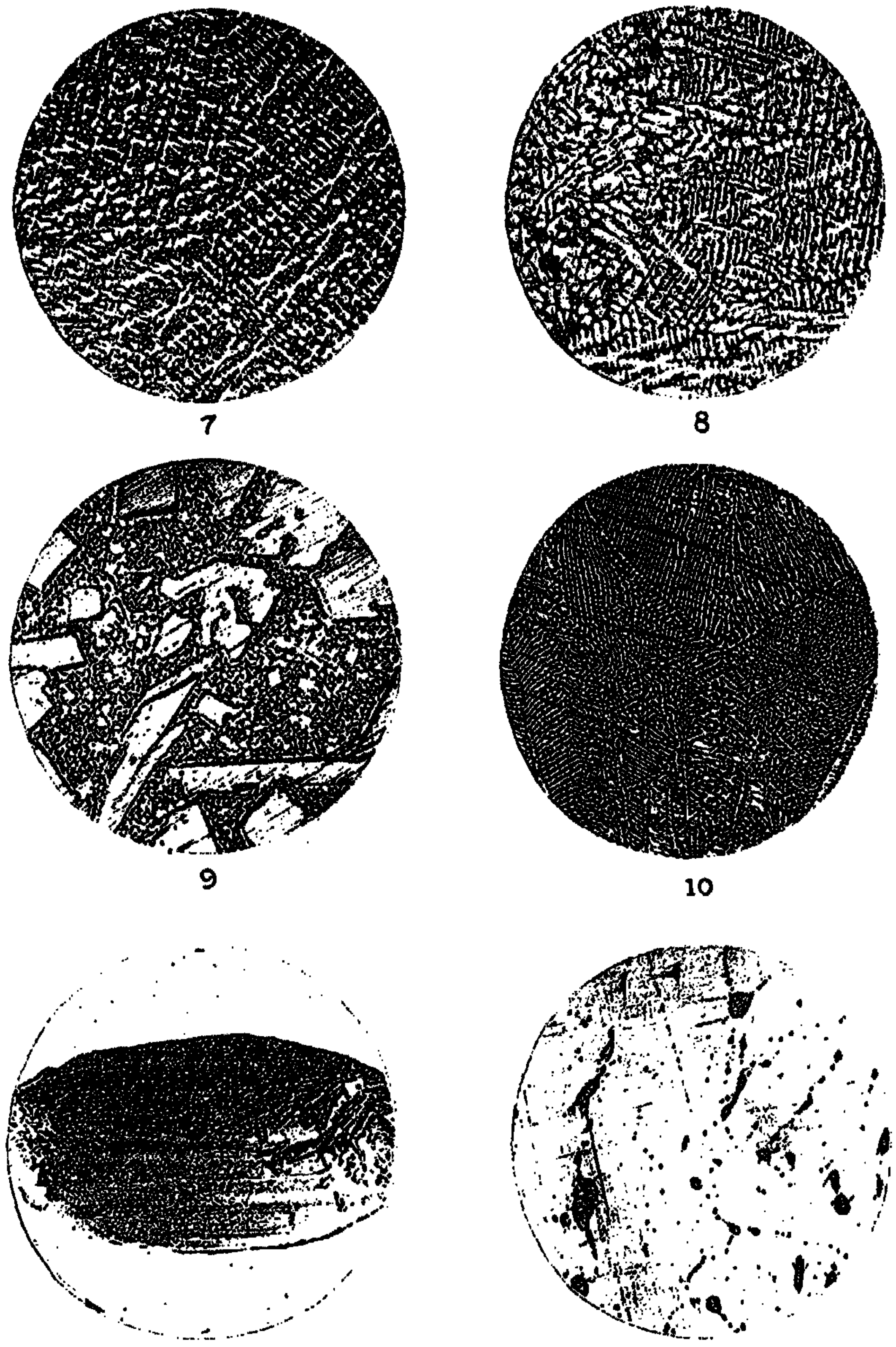
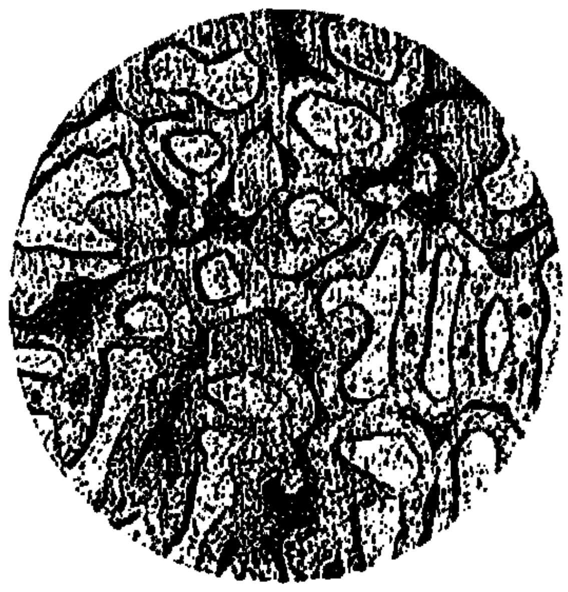


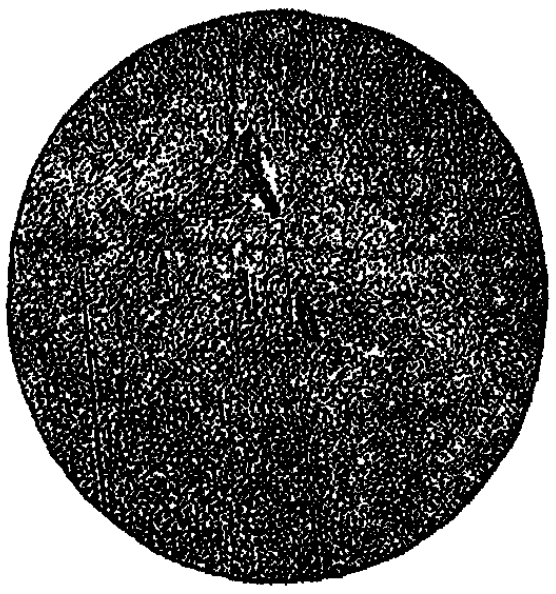
PLATE II. Photomicrographs

This series of photomicrographs was obtained from the cast alloys, slowly cooled, the magnification being 25 diameters.

Photomicrographs 1 to 4 inclusive show clearly the crystals of primary germanium imbedded in eutectic (usually darker than the primary crystals). Photomicrographs 6 to 8 inclusive show light-colored primary crystals likewise surrounded by eutectic, but in these cases the primary crystals consist not of silver, but of a solid solution of germanium in silver, in which the germanium content lies between 6 and 7 atomic per cent. Photomicrograph 5 shows the practically pure eutectic.[1]



13



14

Plate III. Photomicrographs

Photomicrograph 9 brings out the duplex structure of eutectic in which the primary crystals (in this case germanium) are imbedded. It represents Alloy 6 (silver = 38.2 atomic per cent) magnified to 100 diameters (Cf. Photomicrograph 2 for the same alloy at 25 diameters). Photomicrograph 10 shows beautifully the characteristic structure of the eutectic when very highly magnified (250 diameters) and when etched with hydrogen peroxide. Photomicrograph 11 is a section of a cast ingot of Alloy 4 (silver = 19.7 atomic per cent), and shows the segregated crystals of primary germanium in the upper part (magnified to 3 diameters).

We now come to the question of solid solutions. Photomicrograph 13 for Alloy 19 (silver = 93.2 atomic per cent), cast and slowly cooled, consists apparently of two phases. The high magnification (100 diameters) however brings out clearly the fact that the primary crystals are *cored*, that is to say, the crystals are not homogeneous, and the lighter central portions are richer in silver than the slightly darker outer areas, the dark material in the inter-

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[1] Photomicrographs 4 and 6 are distinctly different in structure from the pure eutectic (Photomicrograph 5), though the alloys from which they were taken differ from the eutectic alloy to the extent of only one atomic per cent of silver. The differences, however, are easily sufficient to determine within narrow limits the composition of the eutectic and it is evident that we have here a very satisfactory confirmation of the thermal analysis (Cf. the data for the first arrests in Table I).

stices being eutectic. Since coring may be characteristic of the formation of solid solutions,[1] a solid solution of germanium in silver is indicated.

Photomicrographs of the rapidly cooled alloys high in silver (Alloys 18 to 22 inclusive) all showed cored crystals, proving that the primary crystals consist of a solid solution of germanium in silver. To find the approximate composition of the saturated solid solution at the eutectic temperature, these alloys were next annealed[2] for some hours just below the eutectic temperature, so as to bring the system as a whole into equilibrium. Photomicrographs were then taken from the annealed specimens.

Photomicrographs 13 and 14 show clearly what happened. The former represents the rapidly cooled alloy with its cored crystals surrounded by a little of the eutectic. The latter shows the same alloy after it had been annealed for 240 hours at 640°; it has become practically entirely homogeneous.

These two photomicrographs were taken from Alloy 19 (silver = 93.2 atomic per cent). Alloys 20 to 22 inclusive (all richer in silver) became homogeneous after being annealed, and a special alloy (19A, containing 93.7 atomic per cent of silver) became practically so, but Alloy 18 (silver = 91.2 atomic per cent) did not become homogeneous, the eutectic being plainly visible after long-continued heating at 640°. We can thus conclude with reasonable certainty that the limit for the solid solution lies between 93 and 94 atomic per cent of silver, or in other words that silver saturated with germanium contains between 6 and 7 atomic per cent of the latter metal just below the eutectic temperature.

The possibility of a second solid solution—one of silver in germanium—was investigated in a similar way but not so carefully. The preliminary evidence was all against the existence of such a second solid solution, for indications of cored crystals in the germanium-rich alloys were never found. However, Alloy 1 (Silver = 1.21 atomic per cent) was annealed for 120 hours at 640°. Photomicrograph 12 shows this alloy after being annealed. It is still definitely heterogeneous. Silver therefore appears to be insoluble in crystals of germanium.[3]

Some photomicrographs showed the eutectic to be granular (cf. the eutectic in Photomicrograph 9) and others showed it to be angular (cf.

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[1] Coring is due to the fact that the system is not in equilibrium. If an alloy, which under equilibrium conditions consists entirely of a homogeneous solid solution, be cooled rapidly coring may take place, that component the addition of which to the melt brings about a lowering of the freezing point (in this case germanium) tending to be low in the center of the crystals (the first part to separate out) and high in the outer portions. This segregation may result in the melt passing the limit of composition for the homogeneous solid solution as the solid phase, in which case a certain amount of eutectic will form and there will be a short eutectic arrest. This has happened in the case of Alloy 19.

[2] The alloys on graphite blocks were annealed in purified hydrogen. The thermocouple in a thin-walled quartz tube was placed close to the metal. After being annealed, the specimens were chilled as quickly as possible by removing the upper half of the heating unit of the combustion furnace.

[3] The system silver-germanium is similar in this regard to the system silver-tin. Tin forms solid solutions in silver, but silver does not do so in tin. Cf. Murphy: J. Inst. Met., 35, 107 (1926). On the other hand, silver dissolves slightly in crystals of silicon, but silicon is said not to dissolve in crystals of silver. Cf. Arrivaut: Compt. rend., 147, 859 (1908).

Photomicrograph 10). Whether the eutectic is granular or angular depends upon the rate of cooling and upon the nature of the component which is in excess. Slow cooling (Photomicrograph 10) gives the angular form. When the constituent in excess is the solid solution of germanium in silver, the eutectic appears to be granular under all conditions.

Part III. The Electrical Conductance of the Alloys from Germanium to the Eutectic

At the outset of this investigation it was thought worth while to determine the electrical conductance of the alloys as a further means of aid in interpreting the thermal data and in constructing the equilibrium diagram. It is well known that the conductance-composition data afford a basis[1] for detecting the presence of intermetallic compounds and solid solutions, and enable one to fix for the latter the limiting compositions.

The system silver-germanium is a somewhat unusual one, inasmuch as there is an enormous difference between the conductances of the two components—silver having the highest conductance known and germanium having one of the smallest which is ascribed to a metal, so-called. This fact is brought out in Table II.

TABLE II

The Specific Conductances of Some Metals

Metal	Specific Conductance (0°–25°)
Boron	0.5×10^{-1} (Weintraub)
Silicon	6×17
Germanium	11.2 to 13.3
Graphite	4×10^2 to 20×10^2
Tin	87×10^3
Silver	607×10^3

The conductances of all the silver-germanium alloys were not determined, but enough were measured to establish the general form of the curve between conductance and composition from germanium to the eutectic alloy (silver = 74 atomic per cent). Beyond this point the conductance became so large that, with the experimental equipment then available, it proved to be impractical to carry the work farther. In view, however, of the fact that germanium forms a solid solution in silver it would be interesting and instructive to determine the conductances of the silver-rich alloys.

The conductance bar was prepared by casting the alloy in a mold of aluminum oxide[2] and shaping the cast bar with an abrasive. Segregation was prevented by rapid chilling. The dimensions of the shaped portion of the bar were measured with a Brinell microscope.

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[1] Cf. Tammann: "A Text book of Metallography," 293 (1925).

[2] Cf. Dennis, Tressler, and Hance: Loc. cit.; J. Am. Chem. Soc., 45, 2033 (1923).

In the actual measurement of the resistance of the bar, the latter was held firmly between graphite blocks made to press against the ends of the bar by means of helical springs. The storage-battery current was led first through a standard resistance, thence through the conductance bar, and finally through a variable control resistance. The potential differences were determined with a precision potentiometer.[1]

The conductance data are assembled in Table III.

TABLE III

Conductance Data

Conductance Bar (Number)	Silver Content of Alloy		Specific Conductance	
	Atomic Percent	Volume Percent	Actual	Calculated
(Germanium)	0	0	13.3	13.3
1c	1.08	0.83	59	3000
2	5.50	4.29	398	19000
3c	9.15	7.11	435	33000
4c	18.5	14.7	1157	69000
5	29.2	23.8	1485	114000
6c	31.4	25.6	1905	123000
7c	58.3	51.6	7190	249000
8	60.2	53.5	8656	258000
14(eutectic)	74.0	68.4	14100	332000
(Silver)	100	100	(607000)[2]	607000

In addition to the conductances as actually measured, this table contains for comparison values calculated on the assumption that the specific conductance of a binary alloy should be a linear function of its composition by volume, in accordance with the law of simple mixtures.[3] These calculated values appear in the last column of data.

Regarding the relation between conductance and composition, Jeffries and Archer[4] say:—"In alloys which are aggregates of two or more constituents it is a fairly general rule that the specific conductivity is a linear function of the composition by volume. That is, an alloy functions electrically as though its various constituents were grouped as continuous parallel conductors. This rule is perhaps never more than approximately true, and there are some exceptions of a very marked nature. It is obvious for example that an alloy which contains a constituent of very low conductivity, in the form of a continuous network, will be a poor conductor as a whole, no matter how high the conductivity of the discontinuous constituent

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[1] Each end of the shaped part of the conductance bar was encircled accurately with a narrow groove and in this groove a fine platinum wire was tightly twisted. This wire was connected to the terminals of the potentiometer.

[2] Not measured in this work.

[3] Cf. Jeffries and Archer: "The Science of Metals" 338 (1924); Ruer (Mathewson): "The Elements of Metallography," 242 (1909); Roozeboom: "Die heterogenen Gleichgewichte," 2, 186 (1904).

[4] Loc. cit.

within the network. There is, then, a condition which is analogous to a series connection rather than a parallel connection, and the resistance of a number of conductors arranged in series is equal to the sum of the individual resistances. Even with this type of structure, however, the general rule holds approximately if the specific conductivities of the various constituents do not differ greatly."

Unfortunately, the conductance of the second physical constituent in the silver-germanium alloys—i.e. the silver-rich solid solution—was not measured for the reasons which have been stated, so it is not possible for us properly to test the rule referred to in the preceding quotation. However, unless the germanium in the saturated solid solution produces an enormous decrease in the conductance of the silver—something which of course is not impossible—it seems probable that the alloys possess an abnormally small conductance and do not come even close to following the rule mentioned by Jeffries and Archer. One may therefore conclude, not unreasonably, that the alloys which we have investigated consist essentially of a network in which the continuous constituent is a poor electrical conductor, and therefore must be the germanium.[1]

The conductance data for these alloys are not of much help in fixing the limits for the formation of solid solutions. In accordance with the rule first enunciated by Le Chatelier,[2] the addition of a second component in increasing increments causes the electrical conductance to pass through a *minimum* if a solid solution is formed. Since there is no minimum in the conductance as one adds silver to germanium, there is no indication in the conductance data that silver forms a solid solution in germanium. In view of the exceedingly small conducting power of germanium and the extremely great conducting power of silver, it seems scarcely likely, however, that there would be a minimum conductance even if a solid solution were formed, and so the conductance data should not be considered as conclusive evidence one way or the other. It is best to place chief reliance on the microscopic evidence, as we have done.

Owing to experimental difficulties the conductances of the silver-rich alloys, in which there is without doubt a solid solution, were not measured. The Le Chatelier rule would undoubtedly hold here, and we should expect to find the saturated solid solution (Alloy 19 or 19A) having a relatively small conductance, even though it contains from 93 to 94 atomic per cent of silver. This point should be investigated.

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[1] There are many familiar instances of low conductance when one constituent is a poor electrical conductor. For example, sulphur lowers the conductance of copper out of all proportion to the quantity added because the poorly conducting sulphide which is formed coats the crystals of copper and so renders them to some degree discontinuous. Likewise when coarse particles of tungsten are coated with fine particles of thoria, the compressed mixture conducts poorly, but on the other hand, if coarse particles of thoria are coated with tungsten, the mixture conducts well. Cf. Fink: Met. Chem. Eng., **15**, 404 (1916). We have a similar thing with gels of the colloidal metals. Cf. Briggs: J. Phys. Chem., **17**, 292 (1913).

[2] Cf. Ruer (Mathewson): "The Elements of Metallography," 243 (1909).

Part IV. Discussion and Miscellaneous Observations

The characteristic sprouting of germanium diminished as silver was added. After Alloy 4 no further sprouting was observed. Likewise the alloys became steadily less brittle as the silver content increased. It was impossible to fracture the eutectic alloy in a mortar.

The measurement of the tarnish-resistance, to which reference has already been made in this paper, was carried out by the Bureau of Standards through courtesy of Dr. H. W. Gillett. The results which were obtained, however, were not favorable, since the addition of germanium appeared to increase rather than to diminish the rate of tarnish of silver in the sodium polysulphide solution which was used in the tests.

The results of this investigation show that the alloys of silver and germanium form a simple eutectiferous series between the limits of 0 and 93-94 atomic per cent of silver, the two phases being germanium and a solid solution of germanium in silver, the latter containing 6 to 7 per cent of germanium when saturated at the eutectic temperature (650°). There is no indication of silver-germanium compounds in the solid.

We shall now compare the system silver-germanium with the systems silver-silicon and silver-tin, for both of which the equilibrium diagrams have been determined.[1] According to the most recent work on silver-silicon (by Arrivaut in 1908), this system is also a simple eutectiferous series between a solid solution and one of the pure components, in this case silver. However, as Arrivaut relied upon purely thermal evidence (disappearance of the eutectic arrests) and did not supplement this with microscopic and other evidence his conclusions about the formation of solid solutions are unreliable. One can see, nevertheless, that the system silver-silicon is similar to the system silver-germanium, which is exactly what one would expect.

The question whether silver and silicon form compounds was for long a matter of dispute. In 1858 Wöhler[2] passed silicon hydride through a solution of silver nitrate and obtained a black precipitate which he thought was silver silicide. In 1889 Warren[3] heated potassium silico-fluoride, metallic sodium, and silver and obtained what he regarded as silver silicide. DeChalmot[4] also thought he had prepared the compound by heating sand, lime, charcoal and silver. On the other hand Moissan,[5] as well as Vigoureux[6] denied the existence of silver silicide, and their position seems to have been justified by the work of Arrivaut.

In view of the similarity which exists between silicon and germanium, one would not expect, therefore, to find a silver germanide. The equilibrium diagram reported in this paper gives no evidence of such a compound or

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[1] Cf. Arrivaut: Comptes rend., **147**, 859 (1908); Murphy: J. Inst. Met., **35**, 187 (1926).

[2] Ann. Chim. Phys., **54**, 222 (1858).

[3] Chem. News, **60**, 5 (1889); **67**, 95 (1896).

[4] Am. Chem. J., **18**, 95 (1896).

[5] Comptes rend., **121**, 625 (1895); **138**, 1299 (1904).

[6] Comptes rend., **144**, 1214 (1907).

compounds, and in the light of the outcome of the controversy about silver silicide, we feel sure that no compound has been missed in our work.

Murphy's investigation of the silver-tin alloys is very complete. It indicates three solid solutions and a eutectic between the gamma solution and pure tin. The gamma solid solution exists between very narrow limits of composition and Murphy considers it to contain an intermetallic compound having the formula Ag_3Sn. As a matter of fact there is very little evidence that this compound really exists.

If Ag_3Sn be excluded because of insufficient evidence, it may be stated that neither silicon, nor the sub-group consisting of germanium, tin, and lead, forms compounds with silver. This fact is in accordance with Tammann's[1] well-known second rule, which states that an element in general either forms compounds with all the members of a given sub-group in the Periodic Table, or else it forms compounds with none.

The various systems with silver show that germanium is intermediate between silicon and tin, just as it should be. Silver may hold in solid solution 26 atomic per cent of tin, 7 atomic per cent of germanium, and 0 atomic per cent of silicon.[2] Germanium and tin are unable to hold any appreciable quantity of silver in solid solution, and it seems highly probable, therefore that Arrivaut's solution of silver in silicon is doubtful. In all three systems the liquidus curve is of the same, or nearly the same, simple type.

Germanium appears to resemble silicon more than it does tin as regards the type of crystals which it forms in these alloys. The primary crystals of germanium appear in the photomicrographs to have clear-cut crystallographic faces. This is also characteristic of silicon but is not so of tin.[3]

Part V. Summary

The salient features of this paper may be summarized as follows:

(1) The equilibrium diagram for the system silver-germanium has been determined for temperatures between 600° and 1000°.

(2) The diagram is based both on thermal and metallographic data.

(3) The solid phases in equilibrium with the melt are pure germanium and a solid solution of germanium in silver. The latter when saturated contains between 6 and 7 atomic per cent of germanium at 650°.

(4) Germanium and silver form no stable compounds at these temperatures.

(5) The alloys form a simple eutectiferous series. The eutectic temperature is 650° and the eutectic composition is 74 atomic per cent of silver.

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[1] Z. anorg. Chem., 49, 113 (1906); 55, 289 (1907).

[2] Though Arrivaut does not recognize a solid solution of silicon in silver, he would probably have overlooked a dilute one had it been formed, since he relied entirely on thermal data.

[3] Note the photomicrographs for the system silicon-magnesium given by Vogel: Z. anorg. Chem., 61, 46 (1909), compared with those for lead-tin by Degens: Ibid., 63, 207 (1909).

(6) The specific electrical conductance of some of the alloys has been measured. The conductances are surprisingly low and the conclusion is drawn that in the fine-structure of these particular alloys germanium predominates as the continuous phase.

(7) The system silver-germanium has been compared with the systems silver-silicon and silver-tin. Germanium is intermediate between silicon and tin as regards the properties of the silver alloys.

(8) The authors wish to express their indebtedness to Professor L. M. Dennis, who placed at their disposal the supply of germanium which made this investigation possible, and also to Professor C. W. Mason for assistance in the metallographic work.

Cornell University
March, 1929

AN ATTEMPTED MEASUREMENT OF THE PARTITION COEFFICIENT OF A COLLOID, GELATINE, BETWEEN TWO LIQUIDS

BY ROWLAND MARCUS WOODMAN AND PATRICK HUGH GALLAGHER

Not many cases are known where a colloid is appreciably soluble to give some type of solution, pseudo or true, in two liquids which are immiscible or nearly so; the system cresylic acid-gelatine-water, however, furnishes an example.

Gelatine is soluble in water to give a characteristic colloidal solution; it is also soluble in the mixture of cresols known as cresylic acid,[1] but whether or not this solution is true or pseudo, or is due to the formation of complex compounds such as cresates, is a moot point at present. Since the authors had not the facilities for solving this question, it was tacitly assumed *as a starting point* that the solution was true, and hence the problem presented itself as the distribution of a solute between two liquids with one of which it forms a true solution, and with the other, a colloidal solution.

It will readily be perceived that as the determination of the partition coefficient of a substance necessarily entails shaking together the two immiscible liquid solvents and the common solute, difficulties will be encountered because of the tendency to emulsion formation when that solute is a colloid; the present system yields emulsions, and the method used for surmounting this difficulty will be detailed later.

Experimental and Results

Emulsion formation in this system has been investigated previously, and has been found to be complicated by the formation of dual types, sometimes even when the relative proportions of the three constituents are kept the same.[2] The experiments were extended to include these complications in the hope that knowledge of the mechanism of the formation of emulsion types would be gained.

The former experiments demonstrated that cresylic acid-in-water emulsions, especially when prepared directly, were usually unstable, (probably owing to the presence of unemulsified acid), cracking and completely separating into two layers in from 6-24 hr.[2]

Advantage was taken of this fact: emulsions were made by gentle partial rotation[2] of 50 c.c. lots of an aqueous solution of Coignet's Gold-Label gelatine (the solution containing a known amount of nitrogen), with 50 c.c. lots of cresylic acid in 100 c.c. cylinders, followed by vigorous shaking to ensure

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[1] Stocks: "Brit. Ass. Colloid Reports," 1, 74 (1917).

[2] Woodman: J. Phys. Chem., 30, 658 (1926).

partition.[1] Acid-in-water emulsions resulted; these—in general even more unstable than corresponding emulsions obtained in previous experiments,[2] no doubt because the gelatine used had once, during its history, been heated at 100°C. for some time to dry it—broke usually in 1/2-1 hr., and were allowed to separate out completely in a thermostat maintained at 13.5 ±0.25°C., nitrogen determinations then being made on definite volumes of the clear layers.

In parallel experiments, the water-in-acid type of emulsion was made by known methods,[2] and, after allowing a sufficient period of time for full "creaming," (which creaming, in the case of this type, is upwards, as cresylic acid is denser than the water-in-acid emulsion cream[2]), samples of the acid underlayer were analyzed for nitrogen; in these experiments, of course, estimation of the nitrogen content of the aqueous phase was impossible, as the water was wholly emulsified, the water-in-acid type being the perfect and stable form of this system.[2] In the case of this type also, a small amount of the gelatine must have been adsorbed at the dineric interfaces of the emulsion cream.

The work on the water-in-acid type was conducted with the notion of ascertaining if any significant difference existed in the concentrations of gelatine in the acid layers for the two types, thus indicating, indirectly, whether or not alternative distributions of the colloid were possible in the system.

Estimation of nitrogen: Analysis for nitrogen, which is the best method of estimating such a substance as gelatine, was carried out by the following methods: initial emulsifying media of aqueous gelatine and aqueous layers of completely cracked emulsions were treated by the direct Kjeldahl process. Cresylic acid layers gave more trouble, and, after repeated tests, it was found that the nitrogen could be estimated with certainty only after distilling off the acid in steam; this was done as follows: about 40-50 c.c. of the acid layer were placed in a 650 c.c. Pyrex Kjeldahl "cooking" flask, a little dilute sulphuric acid added to trap any evolved ammonia, and the acid was distilled off in steam. By regulating a flame placed under the flask, it was found possible to finish the steam distillation with a residue of about ten c.c. of clear aqueous medium, a straight forward Kjeldahl, using the same flask for the "cooking," then following.

Blank experiments made for the purpose of correcting the various results obtained were: (1), the ordinary Kjeldahl blank, the processes of "cooking" and distillation being conducted in the absence of added nitrogen, in order to correct determinations made on the initial aqueous gelatine solutions used; (2), a similar blank using 35 c.c. of water saturated with cresylic acid at 13.5°C., corresponding to nitrogen measurements made on aqueous *layers;* (3), on the steam distillation, "cooking" and ammonia distillation of 50 c.c. of cresylic acid saturated with water at 13.5°C., corresponding to the cresylic

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[1] At first these emulsions were made in five lots of 20 c.c. each, to correspond exactly with the treatment given in the previous investigation.[2] Later, it was found that 50 c.c. lots of each phase could be used without any effect on the type formed.

[2] Woodman: loc. cit.

acid-layers; and, (4), similar to (3), using 25 c.c. of water-saturated cresylic acid instead of 50 c.c. The difference between (3) and (4), a very small blank, then corresponded to 25 c.c. of water-saturated cresylic acid going through the process of steam distillation, "cooking" and ammonia distillation.[1]

The results are given in Table I:

Notes on the preparation and treatment of the emulsions:

Emulsions 1, 2 and 3: Gelatine solution 0.0615% as regards N_2, and 47 hr. old. The temperature of preparation and storage of the emulsions was 25°C.; at this temperature, all methods of treatment seemed to give the W in C type,[2] no doubt because of the fact that heating of a gelatine solution may be regarded as a reversal of the ageing effect, 25-39°C. seeming to be a rather critical range of temperature.[3] The C in W type, therefore, was made indirectly by re-shaking a W in C type.[3]

Subsequent experiments were conducted in a thermostat at 13.5 ± 0.25°C., to avoid this possible temperature effect.

Samples of the cracked layers from the C in W type (no. 1), were separated for analysis after 7 hr. The cresylic acid continuous phases of the W in C emulsions (nos. 2 and 3), were analyzed after allowing 31 hr. for full creaming.

Emulsions 4 and 5: Age of gelatine solution (0.0615% N_2), 51 hr. Temperature 13.5°C. Emulsions (W in C), allowed 27 hr. for creaming.

Emulsions 6, 7, 8 and 9: Gelatine solution (containing 0.0615%N_2), 72 hr. old. Temperature 13.5°C. Originally 6 and 7 were perfect W in C types, which creamed, and 8 and 9 C in W types, which completely cracked and separated in 30 min. They were stood at 13.5°C. for 216 hr., and were then vigorously re-shaken, all four giving the C in W type.[3] No. 8 gave, on re-shaking, a perfect C in W emulsion, a result obtained on two occasions in previous investigations,[3] the other three giving the usual unstable C in W type. This perfect C in W type showed great stability, indicated by the very slow creaming (*downwards*); it was hoped that the emulsion would cream completely, and that a nitrogen estimation on the supernatant excess continuous aqueous phase might show a significant difference from estimations got from aqueous layers of cracked C in W emulsions, where diffusions of gelatine might take place during the time allowed for the layers to exhibit non-turbidity. Unfortunately, the creaming was so slow that, even after 48 hr., when traces of acid due to cracking began to appear, the lower portions of the supernatant aqueous phase were still very milky and unfit for sampling; in 96-120 hr. the emulsion was entirely cracked, and, therefore, all four experiments resolved themselves into analyses of the cracked layers.

Emulsions 10, 11 and *12:* Gelatine solution (0.0615%N_2), 216 hr. old. Temperature, 13.5°C. Nos. 10 and 11 were C in W, and no. 12 was W in C.

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[1] Nitrogen could not be detected in the cresylic acid by carefully-conducted Lassaigne's tests.

[2] W in C indicates water-in-cresylic acid, and C in W cresylic acid-in-water, emulsions.

[3] Woodman: loc. cit.; J. Agric. Sci., **17**, 44 (1927); J. Phys. Chem., **33**, 88 (1929).

No. of Emulsion:[1]	Aq. Gelatine Used:			Total Vol.[2] of System (c.c).	Vol. of Acid Layer (c.c.)	Vol. of Aq. Layer: (c.c)	Type of Emulsion at Time of Analysis:[3]	%N₂ in Acid Layer:	%N₂ in Aqueous Layer:	Total N₂ Used in System in Gm.:	Total N₂ Found by Calculation from the Experimental results in the System in Gm.:
	%N₂:	Vol.[2] in c.c.:	Age in hr.:								
1	0.0615	—	47	—	—	—	C in W	0.0524	0.0007	—	—
2	"	—	47	—	—	—	W in C	0.0517	—	—	—
3	"	—	47	—	—	—	"	0.0518	—	—	—
4	"	—	51	—	—	—	"	0.0494	—	—	—
5	"	—	51	—	—	—	"	0.0490	—	—	—
6	"	—	72	—	—	—	C in W	0.0500	0.0010	—	—
7	"	—	72	—	—	—	"	0.0480	0.0005	—	—
8	"	—	72	—	—	—	"	0.0472	*see*[4]	—	—
9	"	—	72	—	—	—	"	0.0507	0.0012	—	—
10	"	—	216	—	—	—	"	0.0500	0.0008	—	—
11	"	—	216	—	—	—	"	0.0526	0.0006	—	—
12	"	—	216	—	—	—	W in C	0.0513	—	—	—
13	"	50	504	100	55.9	44.1	C in W	0.0525	0.0006	0.0308	0.0296
14	"	50	504	100	—	—	W in C	0.0516	—	—	—
15	0.0305	50	24	100	55.8	44.2	C in W	0.0269	0.0004[5]	0.0153	0.0152
16	"	50	24	100	—	—	W in C	0.0262	—	—	—
17	0.0977	50	24	100	—	—	"	0.0832	—	—	—
18	"	50	24	100	55.5	44.5	C in W	0.0837 0.0823	0.0012	0.0488	0.0466
19	0.0610	50	24	100	—	—	W in C	0.0528	—	—	—
20	"	50	24	100	55.8	44.2	C in W	0.0543	0.0002	0.0305	0.0304
21	"	50	24	100	—	—	W in C	0.0534	—	—	—
22	"	50	24	100	—	—	"	0.0532	—	—	—
23	"	50	48	100	56.2	43.8	C in W	0.0518	0.0005	0.0305	0.0293
24	"	50	48	100	55.0	45.0	"	0.0536	0.0008	0.0305	0.0298

[1] Nos. 1, 2 and 3 at 25°C.; others at 13.5°C.
[2] In experiments without figures in these columns, the vols. of both phases were approximately 50 c.c. before emulsification.
[3] Details of the ages of the emulsions themselves on analysis are given in the text.
[4] This was the very stable C in W type (see text); the aq. layer was too turbid for analysis.
[5] Sample spoilt during estimation; result got by calculation from the solubility of the acid in the water (see later)

The C in W type, which broke completely in 1/2 hr., were separated as quickly as was consonant with non-turbidity of the layers (3 hr.), in the hope that any redistributions of gelatine taking place after cracking by diffusion processes, *etc.*, might be averted to some extent. No. 12 was also sampled as soon as the acid continuous layer was quite clear (24 hr.).

Emulsions 13 and 14: Gelatine solution (containing 0.615% N_2), 504 hr. old. One emulsion of each type was made; previous experiments had demonstrated[1] that with a two months' old solution of gelatine of similar concentration, the C in W type is alone possible, however vigorous the shaking given (by hand), and it was thought that some difference in distribution of the gelatine might be noticed in preparing the two types of emulsions from an aged solution of gelatine which was not, however, so old as to give the one type only. Gentle treatment was not necessary here to produce the C in W type; in fact, the shaking given in both cases was apparently exactly similar, and the formation of the W in C type must have been, to some extent, accidental. No. 13 (C in W), was separated after 17.5 hr., and the acid layer of 14 (W in C) was sampled after 24 hr.

Emulsions 15, 16, 17, 18, 19, 20, 21, 22, 23 and 24: These experiments, all at 13.5°C., were made with a new set of gelatine solutions of varying concentrations, so that differences in distribution of gelatine when varying amounts of gelatine were present in the system could be noted.

The volumes of the liquid phases used for making the emulsions were in all cases exactly 50 c.c. (this applies also to emulsions 13 and 14), and the C in W types were prepared in cylinders calibrated as perfectly as possible, so that the volumes of the cracked layers could be read with tolerable accuracy; thus, by comparing the gelatine actually used in the experiments with that found by calculation from experimental data, some notion of the trustworthiness of the methods of estimation was obtained.

No. 15 was a C in W, and no. 16 a W in C type, prepared by using in each case 50 c.c. of a 24 hr. old solution of gelatine containing 0.0305% N_2; the layers of 15 were analysed after 6.5 hr., and the acid underlayer of 16 after 28 hr.

Nos. 17 (W in C) and 18 (C in W), were similarly prepared using 24 hr. old gelatine solution containing 0.0977% N_2; the acid underlayer of 17 was allowed 72 hr. to clear, and the cracked layers of 18, 26 hr.

Nos. 19, 20, 21, and 22 were respectivly W in C, C in W, W in C and W in C types, analyzed 72, 2, 69 and 70.5 hr. after making, made similarly from a 24 hr. old solution of gelatine containing 0.0610% N_2.

Extraordinary care had to be exercised in preparing the C in W types with all concentrations of gelatine in these last experiments, possibly owing to the newness of the solutions (24 hr.)[1]. Nos. 23 and 24, however, both C in W types made similarly by using the 48 hr. old solution containing 0.0610% N_2 (the layers being separated after 2.5 and 2.75 hr. respectively), were easier of preparation, evidently because of the greater age of the gelatine solution.[1]

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[1] Woodman: loc. cit.

Discussion of Results and Theoretical

In previous papers,[1] the hypothesis has been put forward that the type of emulsion formed in a system is regulated to some extent by the partition of the emulsifier between the two liquid phases, this partition favouring that liquid phase which is the usual external phase. The emulsifier may be soluble in either or both of the phases to give some kind of solution, true or colloidal, or, in the limit, may be merely wetted by one or both of the phases, preferential wetting then determining which liquid will be the external phase. (On the assumption that no substance is absolutely insoluble in a liquid, and that, therefore, wetting of a solid surface involves solution, then a partition coefficient must exist, and will be in favour of that liquid which wets preferentially).

The type of emulsion formed in systems capable of yielding dual types may then be influenced in two ways: in the first place, suppose the partition coefficient to be greatly in favour of one phase (as is probably the case in all emulsion systems); then increase in the volume of the phase less rich in emulsifier (assuming other amounts in the system kept constant, and that the ordinary laws of partition—and, in particular, the simple law— hold for colloid solutes), will result in relatively small changes in concentration in both phases and in absolute amount (decrease) of emulsifier in the richer phase, and a small but relatively large change in absolute amount (increase) in the less rich phase. Thus, although the partition coefficient remain constant, the ratio of *total* amounts of emulsifier in the phases will alter considerably in favour of the less rich phase; this change, taken in conjunction with the greater smashing action of the less rich phase due to increase in its volume (dilute emulsions are always more easily formed than concentrated emulsions, intermittent shaking or "mayonnaise" methods having often to be resorted to in making the latter[2]), may cause a type of emulsion in which the phase less rich in emulsifier is the external phase; alteration of the phase volume ratio in the other direction would favour the other type.

In the cases where the constituents of a system, though present in the same proportion, can, by different mechanical treatments, ageing of one phase or of the system, re-shaking, *etc.*, give rise to both types, then some temporary or permanent new partition can be inferred, possibly from some such cause or combination of causes as alteration in pH, alteration in colloidal properties or state of the emulsifier if a colloid, temporary prevention of the establishment of the true partition due to adsorption, *etc.*, or formation of new emulsifiers by reactions taking place in the system. These differences in partition may be quite significant, and yet unmeasurable chemically, for experience teaches that much the greater proportion of the emulsifier is present in one phase, a very small absolute change in the amount in the other phase thus producing a finite difference in the partition coefficient.[3]

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[1] Woodman: loc. cit.: J. Phys. Chem., 33, 88 (1929).

[2] Briggs: J. Phys. Chem., 24, 120 (1920); Woodman: J. Pomol. Hort. Sci., 4, 95 (1925).

[3] Woodman: J. Phys. Chem., 33, 88 (1929).

Clayton[1] has stated with regard to the system now under experiment, and in support of the view that a given emulsifier can promote only "*one* type of emulsion with any two given liquids to be emulsified," that the colloidality of the solutions used is open to investigation, and that the relative amounts of gelatine-water and gelatine-cresylic acid complexes present in the system may play some part, as they may be alternative emulsifiers. These legitimate criticisms were anticipated and dealt with to some extent previously.[2] It is generally conceded that an aqueous solution of gelatine is colloidal; thus though gelatine can exist in water, like a crystalloid, as solutions of single molecules, it can also be associated to a great extent even in very dilute solution.[3] Moreover, it may be postulated that the single molecule of a protein "is sufficiently large to show the beginnings of properties associated with matter in the mass, *i.e.*, the molecules possess surface and form a dispersed phase in the solution,[4]" and, for this reason, it has previously been stated that a so-called *true* solution of gelatine (molecular weight 10,300[5]),—in the sense that the solute is not associated to any great extent—such as cresylic acid gelatine might be, will exhibit colloidality.[4] This reasoning, of course, can be applied with greater weight to any *complexes* of gelatine found in the system. Finally, Clayton[6] expresses the view that an "emulsifying agent must be colloidal in nature,"a generally accepted opinion.[7] It might, therefore, be better to amend the previously-expressed aim of these experiments, and state that it refers to the partition of a colloid between two liquids with which colloidal solutions are formed.

The second comment of Clayton (loc. cit.), referring to the possible formation of gelatine complexes,[1] is much more difficult of proof or refutation, but a great deal can be said in its favour; as, however, work is now being carried out with the ultimate notion of definitely fixing the emulsifier or emulsifiers in this system, and as the object of the present experiments is not related in any great degree to this question, argument for or against this comment will be left to the future. Suffice it to say here, that, even if complexes of any kind are formed, a partition (or equilibrium) of emulsifier or emulsifiers must exist to give the experimental elasticity possessed by the system; as it is usual[8] in *all* cases of partition to express the coefficient as the ratio of some powers of the concentrations of the *dry solute itself* in the phases, irrespective of the possible combination of solute and solvent, or of association of solute (so long as the complex does not settle out as a separate phase), this treatment is followed here.

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[1] Clayton: Emulsions and Their Technical Treatment," p. 31 (1928).

[2] Woodman: loc. cit., p. 669.

[3] Jordan Lloyd: "Chemistry of the Proteins," p. 157 (1926).

[4] Jordan Lloyd: "Chemistry of the Proteins," p. 210 (1926).

[5] Jordan Lloyd: Biochem. J., 14, 147 (1920); 16, 530 (1922); Cohn, Hendry and Prentiss: J. Biol. Sci., 63, 721 (1925).

[6] Clayton: "Emulsions and Their Technical Treatment, p. 126 (1928).

[7] Woodman: loc. cit., p. 669.

[8] Taking a few random cases, partition coefficients of alcohol, pyridine, acids, gases such as ammonia, sulphur dioxide, etc., and anhydrous substances which form hydrates, between water and an immiscible solvent, are calculated without reference to possible solute-solvent complexes.

The results given in Table I indicate that, in this system, any successful and accurate determinations of a partition coefficient will, in view of the experimental difficulties involved, be impossible or extremely difficult. They, however, at the same time, prove conclusively that the partition is greatly in favour of the cresylic acid.

The concentrations found in the acid are as consistent as can be expected, the average of all results at 13.5° for initial aqueous gelatine solutions 0.0615 and 0.0610% as regards nitrogen being 0.0513 ± 0.0005; but, though the range between the extreme nitrogen determinations for aqueous layers is only 0.001% nitrogen, the mean percentage is 0.0007 ± 0.0001, and hence calculation of partition coefficients from single experiments are liable to great variation.[1] These large relative errors are due to the fact that the amounts of gelatine in the aqueous layers are so small as to be inestimable with accuracy, being much smaller than the possible error of estimation.[2]

As the errors in the measurements of the aqueous concentrations are so great, it is useless to expect temporary or permanent variations in the partition, such as the analyses of both types, the re-shaking and ageing experiments, *etc.*, were destined to show; it has been demonstrated elsewhere[3] that these variations would not necessarily be great, and a moderate experimental error might easily swamp them. For this reason, the whole of the results for any particular series was grouped together for treatment.

TABLE II

Concn. of initial 50 c.c. of aqueous gelatine used. (%N_2):	Average concn. of gelatine in cresylic acid (%N_2):	No. of estimations	Average concn. of gelatine in water. (%N_2):	No. of *estimations*	Partition coefft. = $\frac{\%N_2 \text{ in acid}}{\% \text{ in water}}$:
0.0305	0.0266	2	0.0004[4]	1[4]	67(13.5°C.)
0.0615 0.0610	0.0513 ± 0.0005	17	0.0007 ± 0.0001	9	73(13.5°C.)
0.0615	0.0520	3	0.0007	1	74(25°C.)
0.0977	0.0831	3	0.0012	1	69(13.5°C.)

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[1] The standard error of the mean is given throughout, $[\pm\sqrt{(\Sigma d^2/n(n-1))}]$. The probable error of the mean is 0.674 times this.

[2] That nothing is wrong with the methods of estimation, and that the whole fault lies with these small aqueous concentrations, can be perceived by comparing the amounts of gelatine put in the system with those found by experimental data; Table I shows good agreement for those cases where this calculation is possible because of the volumes of the cracked layers of the C in W type being known. The experiments had to be confined to aqueous gelatine solutions of initial concentrations less than 0.1%N_2 approximately because of the possibility of gel formation. The phase volume ratio was not altered in favour of the water, so as to get larger aqueous volumes for analysis), as then the dual types would not have been possible (Woodman: loc. cit.) The formation of different types at other phase volume ratios might be explained either by the formation of gelatine complexes, yielding different emulsifiers, or by the partition hypothesis, as explained previously. *Assuming the first explanation correct, it must necessarily follow on the second,* as an excess of either solvent would indicate a greater total amount of gelatine in association with that solvent in a free or combined state, and hence an equilibrium in favour of that solvent as continuous phase.

[3] Woodman: J. Phys. Chem., 33, 88 (1929).

[4] Calculated by the method shown later.

The actual experimental partition coefficients, assuming the simple law of distribution, and that, therefore, the gelatine is associated to the same extent in both (colloidal) solutions, are as in Table II:

These are quite reasonably near in order of magnitude in view of the experimental difficulties involved, and tend to show that the state of association of the gelatine, whether as complex or not, is the same in both solvents; it should be noticed, however, that an additional aqueous nitrogen determination might, in any of the above series, have destroyed the agreement completely.

Another explanation of the results is evident: the concentrations of the aqueous gelatine are so small as to be negligible, for they fall well within the limits of experimental error, and hence it could be stated that the partition is infinitely in favour of the acid, *i.e.*, that the acid completely extracts the gelatine from its aqueous solution.

In this case it would be difficult to explain the formation of the C in W type by re-shaking unless adsorption from the *internal* phase to the dineric surface were postulated; and that this notion of total extraction by the acid is probably quite erroneous will be perceived from a consideration of the solubility of cresylic acid in water. The cresylic acid used was soluble in water to about 1.5 percent. at room temperature;[1] assuming, therefore, that the solubility of cresylic acid in water in uninfluenced by the presence of gelatine,[2] and that the total concentration of gelatine as gelatine, associated gelatine or gelatine complexes in the *dissolved* acid is essentially the same as that in the cresylic acid *layer*, then the percentage concentration of total gelatine in the aqueous layer will always be 1.5/100 = 1/66.6 of that in the acid layer as a *minimum*.

This means that a definite minimum of gelatine is always present in the aqueous layer, and rules out the possibility of total extraction;[3] if, now, the gelatine in the dissolved acid is in the same state of association as that in the acid layer, so that the simple law of distribution holds, and if the minimum amounts of gelatine so calculated in the aqueous layers are regarded as the true amounts present—these minimum amounts agree very well with the experimental amounts in the fact that they are also much less than any quantity of gelatine which could be measured with accuracy—then the partition coefficient is 66.6 in favour of the cresylic acid phase, a number agreeing reasonably in order of magnitude with the coefficients in Table II calculated wholly from experimental data.

The number 66.6 probably represents as close and fair an approximation to the partition coefficient as is possible in this system; the most that can be

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[1] Woodman: J. Agric. Sci., **17**, 44 (1927).

[2] That this is a reasonable assumption will be perceived from the fact that on shaking 50 c.c. of water at 13.5°C. with 50 c.c. of acid at 13.5°C., the volumes of the resulting layers were 55.8 c.c. (acid) and 44.2 c.c. (aq.); these agree well with data got in the presence of gelatine (see Table I).

[3] In many cases where the partition coefficient is greatly in favour of one liquid, it might be that most of the solute in the other liquid is mainly due to mutual solubility of the liquids.

definitely said is that the cresylic acid layer contains nearly the whole of the gelatine (or gelatine complex), despite the fact that there is no known limit to the solubility of gelatine in water to a colloidal system of some type.[1] This might account for the stability of the W in C type; whether or not temporary or permanently different partitions account for the occurrence of the C in W type in certain circumstances is still an open question.

Summary

An attempt has been made to measure the partition of the colloid gelatine between the two solvents water and cresylic acid.

The system is complicated by the fact that it yields emulsions and, in certain cases, dual types of emulsions by mere mechanical differences in preparation, by ageing effects, by re-shaking, *etc.* A partition hypothesis of the mechanism of the formation of these emulsions and of the dual types is given.

From a survey of the experimental and theoretical evidence, it is concluded that the solute is in a colloidal condition in both solvents. The problem, therefore, resolves itself into the partition of a colloid between two liquids with which it yields colloidal solutions.

The experimental errors are so great as to preclude the possibility of determining whether any significant temporary or permanent difference in partition accounts for the formation of the two types, and hence the series of results were grouped together for treatment.

The partition coefficient, calculated on the simple partition law, is largely in favour of the cresylic acid; so much so that, as the amounts of gelatine in the aqueous phases are small enough to be within the limits of experimental error, any calculations of the coefficient are liable to be subject to great variations. Experimental values for two different concentrations of gelatine in the system 13.5°C. are, however, 73 and 69 in favour of the acid.

The hypothesis that cresylic acid totally extracts the gelatine from its aqueous solution is shown to be untenable. On the supposition that the mutual solubility of the two solvents is responsible in the main for the partition, the value 66.6 in favour of the acid is obtained. This is probably a fair approximation to the truth, and agrees with experimentally-determined values.

The stability of the W in C, and the unstability of the C in W, types, are explained from the fact of the partition coefficient's being so greatly in favour of the acid.

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Jan. 5, 1929.

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[1] Robertson: "The Physical Chemistry of the Proteins," 275 (1918).

THE ADSORPTION OF CERTAIN ACIDS BY WOOL

BY W. W. PADDON

During the course of experiments suggested by Professor Bancroft concerning the dyeing of wool by acid dyes, it was found necessary to obtain data for the adsorption of various acids by wool under the ordinary dyeing conditions. Such data were obtained for sulphuric and hydrochloric acids. Similar data for tartaric acid had been previously determined by Mr. A. W. Bull of this laboratory and are included herein.

The wool used was pure, white sweater, yarn, all of the samples being taken from the same hank. A series of eleven baths of varying concentrations was made up for each acid. One gram of wool was used in each bath, and the adsorption allowed to proceed at the boiling point for one hour, preliminary experiments showing that by this time equilibrium had been reached in every case. The wool entered the boiling bath cold and dry, and was removed hot at the end of the hour. The amount of unadsorbed acid was determined by titrating the bath with NaOH solution using phenolphthalein as an indicator. The data thus obtained are shown in Table I.

TABLE I

Total volume of bath in each case 250 cc. One gram of wool.
Bath heated to boiling for one hour.

Milligram Mols Acid at start	Milligram Mols Acid left in bath	Milligram Mols Acid adsorbed	Milligram Mols Acid at start	Milligram Mols Acid left in bath	Milligram Mols Acid adsorbed
Hydrochloric Acid			Sulphuric Acid		
0.20	0.16	0.04	0.08	0.04	0.04
0.41	0.32	0.09	0.16	0.09	0.07
0.62	0.48	0.14	0.23	0.13	0.10
1.03	0.84	0.19	0.38	0.24	0.14
1.64	1.39	0.25	0.61	0.43	0.18
3.08	2.79	0.29	1.15	0.91	0.24
5.15	4.64	0.51	1.91	1.64	0.27
8.24	7.68	0.54	3.06	2.71	0.35
12.34	11.62	0.72	4.60	4.18	0.42
16.48	15.80	0.68	6.14	5.70	0.44
20.60	19.90	0.70	7.65	7.24	0.41
Tartaric Acid			Tartaric Acid		
0.05	0.03	0.02	1.25	1.14	0.11
0.10	0.08	0.02	2.00	1.88	0.12
0.15	0.12	0.03	3.00	2.86	0.12
0.25	0.20	0.05	4.00	3.83	0.17
0.40	0.34	0.06	5.00	4.83	0.17
0.75	0.67	0.08			

The data are shown in the form of curves, Fig. 1. Milligram molecules of acid adsorbed are plotted against gram molecules of acid left in the bath. It will be noticed that up to concentrations of 2 milligrams per 250 cc., sulphuric acid is slightly more strongly adsorbed than hydrochloric acid. Beyond this point the reverse is true. In all concentrations tartaric acid is much less strongly adsorbed than either sulphuric or hydrochloric acids. There are no abrupt breaks in the curves, indicating that no chemical compounds are formed.

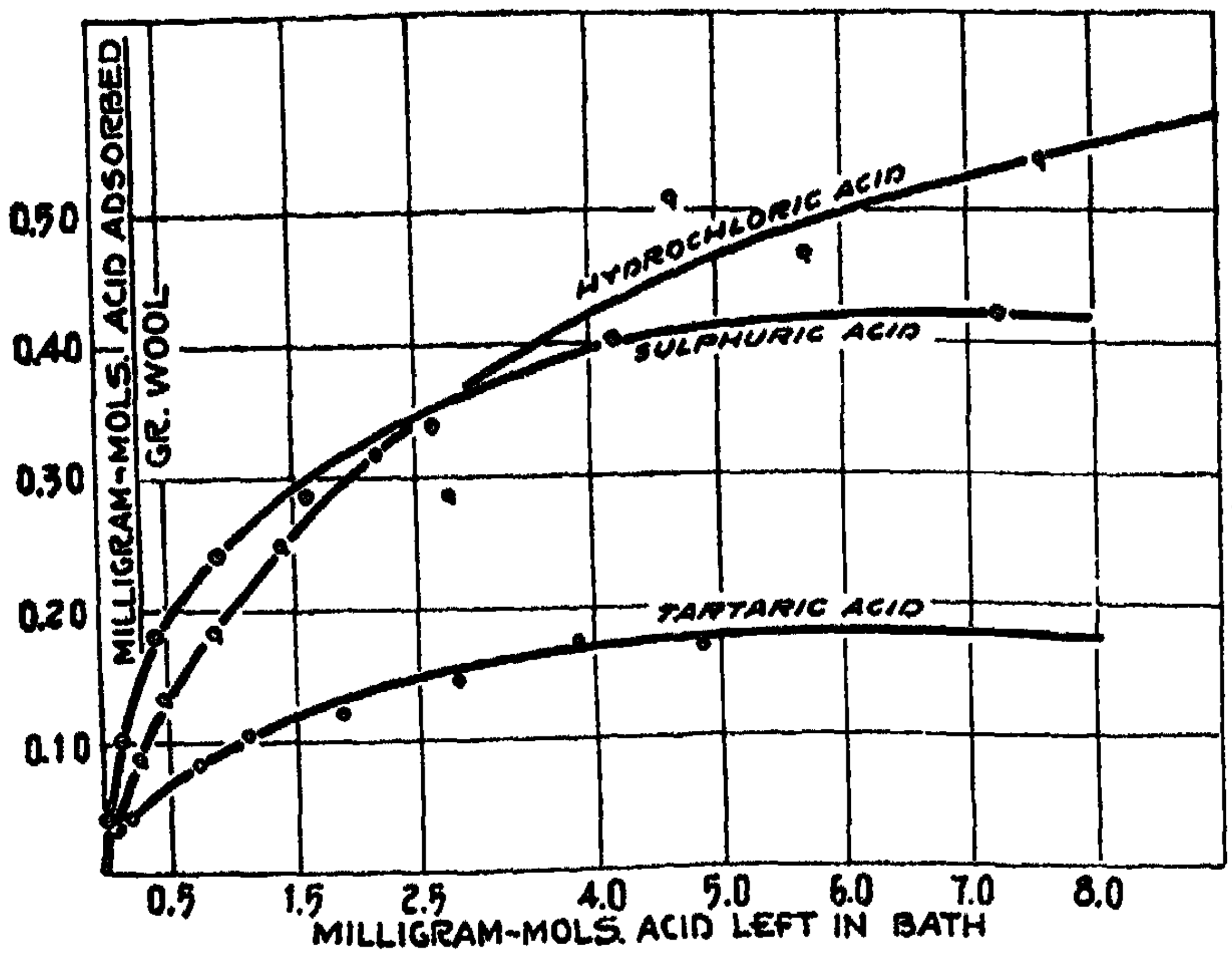

FIG. 1

It is therefore concluded that,

1. At the temperature of boiling water, wool adsorbs tartaric acid much less than it does either hydrochloric or sulphuric acids.

2. In concentrations up to 2 milligram molecules per 250 cc. wool adsorbs at the temperature of boiling water more sulphuric acid than it does hydrochloric acid. Above that concentration more hydrochloric acid is adsorbed.

3. There is no evidence of the formation of chemical compounds between any of the three acids and the wool substance, throughout the range of concentrations experimented with.

I am greatly indebted, for assistance and suggestions to Professor Bancroft, under whose direction these experiments were performed. These experiments were made possible by a grant from the Chemical Foundation.

Cornell University,
June, 1922.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor, Vol. IX. 25 × 16 cm; pp. xiv + 907. London and New York: Longmans, Green and Co., 1929. Price: $20.00.* This volume deals with arsenic, antimony, bismuth, vanadium, columbium, tantalum.

"Arsenic is ubiquitous. Every particle of coal dust or ashes, every-tin-tack, and every metal cooking-vessel is slightly arsenical. Few manufactured food materials or food ingredients are entirely free from it. The glass of white bottles contains it and gives it up to some of the substances stored in them, whence it also enters into food. The Royal Commission on Arsenical Poisoning, recognizing this ubiquity, limited the permissible quantity to 1/100th grain per pound in solid and 1/100th grain per gallon in liquid foods," p. 3.

"Gautier found a small proportion of arsenic normally present in the thyroid glands of all the different animals; 127 grms of human thyroid gland gave 0.95 mgrm. of arsenic. The arsenic in the thyroid gland of a sheep was found to be present in the nucleins, not the peptones; and hence it was inferred that arsenic may possibly form arsenic nucleins like those of phosphorus. Arsenic was also found in the thymus and brain, and only traces in the skin. . . . Arsenic was not found in healthy blood except in the menstrual period when 0.28 mgrm. per kilogram of blood was present. . . . Bertrand and Segale favoured the hypotheses that arsenic is a normal constituent of protoplasm, along with carbon, nitrogen, sulphur, and phosphorus," p. 7.

"According to L. Bloch, the phosphorescence of arsenic at 200°, like that of sulphur and phosphorus, is accompanied by oxidation by which arsenic trioxide is produced. As in the case of sulphur, no ionization occurs, and there is also no formation of ozone, which is produced by both sulphur and phosphorus. The product of oxidation of arsenic, either phosphorescently or with flame, always contains arsenic oxide, just as some phosphoric oxide and sulphur trioxide are always produced in the parallel cases. The arsenic oxide, which may form 1/30th of the whole, seems to be formed direct from arsenic, since arsenious oxide cannot be oxidized under the conditions. It is assumed conversely that arsenic oxide is the sole original product, and this is mainly decomposed into arsenious oxide by a secondary change," p. 26.

"In this part of the world [Styria] when a graveyard is full, it is shut up for about twelve years, when all the graves which are not private property by purchase are dug up, the bones are collected in the charnel-house, the ground is ploughed over, and burying begins again. On these occasions the bodies of arsenic-eaters are found almost unchanged, and recognizable by their friends. Many people suppose that the finding of their bodies is the origin of the story of the vampire," p. 45.

"In the spontaneous oxidation of arsine by oxygen at ordinary temperatures, Reckleben and Lockemann found that arsenic is liberated in a free state, and only the hydrogen is oxidized; when the mixture is exposed to β rays or γ rays, the reaction is accelerated, and arsenious acid is formed, $H_3As + 3O_2 = 2H_3AsO_3$. Since the α-rays are excluded, it is supposed that the oxidation cannot be due to the intermediate formation of ozone," p. 55.

"Kohn found that when copper sulphate is heated with aqua ammonia and arsenic trioxide in a sealed tube at 100°, it undergoes reduction to cuprous salt with formation of arsenic acid. After the resulting cuprous solution has been oxidized to the cupric condition by atmospheric oxygen, estimation of the arsenic acid reveals more of the latter than corresponds with the equation,

$$2Cu^{\cdot\cdot} + AsO_3^{\prime\prime} + 2OH^{\prime} + 2Cu^{\cdot} + AsO_4^{\prime\prime\prime}.$$

Evidently oxidation of the ammonical cuprous solution to the cupric stage activates the atmospheric oxygen for the oxidation of the residual, unchanged arsenious acid," p. 110.

"Dey and Dhar showed that the oxidation of sodium arsenite at ordinary temperature is effected by passing air through a solution in which finely divided copper, cuprous chloride or oxide, zinc, or yellow phosphorus is suspended; finely divided copper dissolves in cold solution of sodium arsenite only in the presence of oxygen. The oxidation of sodium arsenite can be induced by the simultaneous oxidation of sodium sulphite, stannous chloride, *manganous or cobaltous hydroxide: and various aldehydes,"* p. *118*.

The reviewer was glad to see diagrams for the existence of definite compounds on pp. 124, 125, 129, 705, and elsewhere, but, unfortunately, the concentrations of the solutions are plotted as abscissas instead of ordinates. Consequently constant compositions of the solutions give a vertical line and not a flat. It is purely a pedagogical matter; but the present arrangement is bad.

"Arsenic acid is reduced by nascent hydrogen in acid solution as in the case of aqueous solutions of arsenic trioxide; but Covelli said that in alkaline solution it resists reduction under conditions where arsenious acid forms arsine. According to Aschkenasy, if alkaline peroxides be dissolved in arsenic acid, and the solution be evaporated under reduced pressure, at a low temperature, a perarsenate of the alkaline earth is produced. The liquid before evaporation can be converted into a solution of the alkali perarsenate by treatment with alkali sulphate. An alkali perarsenate is produced by evaporating, under reduced pressure, a solution of the arsenate in dilute hydrogen dioxide," p. 144.

"The lead arsenates attracted no special attention until 1893, when F. C. Moulton recommended their use for the destruction of leaf-eating insects. Since then, lead arsenate in different forms has been employed extensively as an *insecticide in place of Paris green*; and several thousand tons are used annually in the United States," p. 189.

Somebody should straighten out the statement, p. 205, that "E. Schweizer found that when an aqueous solution of arsenic trioxide is added to a solution of potassium dichromate, the liquid acquires a fine green colour, and in a few minutes coagulates to a jelly which, dried at 100°, *has the composition* $4K_2O.3CrO_3.3As_2O_3.20H_2O$. *If the liquids be mixed in the* reverse order, the green colour is produced, but no precipitate, p. 205.

"According to S. Delépine, the inhalation of air charged with fumes of arsenic trichloride or the direct application of undiluted arsenic trichloride to the skin causes death rapidly by acute arsenic poisoning. . . . The arsenic is absorbed rapidly by the tissues and *within a few hours can be recovered from most* of the tissues and organs of the body, especially the brain, liver, and kidneys. The symptoms of poisoning by arsenic trichloride include laryngeal obstruction, dyspnoea, and convulsions," p. 245.

"Berthelot obtained a fragment of a vase from some excavations at Tello, and found it to consist of metallic antimony; thus showing that this metal was known to the ancient Chaldeans perhaps 4000 B.C. Forrer reported vessels of antimony from old burial grounds near Tiflis. Helm and Hilprecht, and Mayer found three percent of antimony in some bronze vessels of the oldest Babylonian period; Stoll found antimony in some old Abyssinian alloys; von Parly and Nies observed fifteen percent antimony in some bronzes of the old lake dwellers; Hommel reported antimony in some old Japanese bronzes; Oldenberg in some old Indian bronzes; and Bucher in some old Peruvian alloys," p. 339.

"The part played by antimony in the early history of chemistry is generally overlooked, its claim to an all-important position being over-shadowed by its great rival, gold. There is a considerable amount of evidence, however, that antimony and its compounds must have proved of fascinating interest to many of the early chemists, and it is indeed probable that the study of this metal led to more developments in the early history of the science than did that of the precious metal," p. 341.

"There is a traditional belief with some raisers of cattle that a daily dose of antimony (sulphide) will improve the condition and hasten the fattening of, say, horses and pigs. In Brunswick, for example, the breeders of fat geese add a little antimonious oxide to the food as a traditional custom. The old Roman *pocula emetica*, or everlasting cups, were *made from an alloy containing much antimony*. When wine was allowed to stand therein for a few days, it dissolved some of the metal, and this acted as an emetic, causing any one drinking it to vomit violently. The available evidence is not unequivocal," .p. 385. It seems to the reviewer that more should have been said about antimony trioxide as a mordant than just the reference on p. 386.

The passage on the electrolytic production of stibine, p. 352, is very confused. The reviewer has not yet checked the literature to see whether the difficulty is in the original or in the transcription thereof. What seems to be an interesting photochemical experiment involving monatomic hydrogen is described on p. 396. "According to F. Jones, when stibine is passed over sulphur it is decomposed: $2\ SbH_3 + 6S = Sb_2S_3 + 3H_2S$. The reaction occurs at ordinary temperature only in the presence of light, being slow in diffused daylight, rapid in sunlight. The reaction is also brought about by the electric light, light from burning magnesium, and even the light of a good oil-lamp."

"Berzelius treated a solution of potassium antimoniate with lead nitrate and obtained a white curdy precipitate of lead antimoniate; the same compound was produced by the action of hot nitric acid on an alloy of lead and antimony. The product turns yellow and gives off water when heated. . . . The so-called Naples yellow or *giallolino*, is produced by igniting, in a fireclay crucible for two hours, a mixture of potassium antimony tartrate, with twice its weight of lead nitrate, and four times its weight of sodium chloride. . . . Percy said that he found lead and antimony in the yellow enamel of an enamelled brick from the Kasr ruins of Babylon, and inferred that the colour was due to lead antimoniate. In 1548 Piccolpassi gave instructions for making the colour," p. 457.

"Bismuth hydride is obtained by dissolving an alloy of magnesium with thorium-C or radium-C in 0.2N hydrochloric or sulphuric acid. . . . The results of this and similar experiments show that when magnesium superficially alloyed with bismuth and lead is dissolved in dilute hydrochloric acid, a small fraction of the bismuth is converted into such a state that it can be carried by a gas current through a cotton wool filter, and that a similar reaction does not occur with lead," p. 625. Vanino and Zumbusch were unable to make bismuth hydride electrolytically; but that must be experimental error. Paneth's magnesium-bismuth method is electrolytic in principle and consequently it must be possible to make the hydride electrolytically.

"Bismuth oxychloride and oxynitrate were formerly used as a cosmetic for toilet purposes, but have given way to the cheaper zinc oxide. . . . The oxynitrate, ground with an essential oil is used in imparting an iridescent surface—mother-of-pearl lustre—to pottery," p. 630.

The formula of bismuth oxide has been written at different times as BiO_2, BiO, Bi_2O, and Bi_2O_3, corresponding to atomic weights of 284, 142, 71, and 213 respectively, p. 632. The present atomic weight is 209.

"During the process of the weathering of rocks and ores, a part of the vanadium passes into solution, and becomes concentrated in the limonites like phosphorus, but in smaller proportions. This is illustrated by the fact that bog-iron ores usually contain vanadium. Much of the vanadium is concentrated in sediments as is shown by the wide distribution of vanadium in many sandstones. Vanadium also, accumulates in silts and muds more than it does in the coarser sediments. This is illustrated by the common occurrence of vanadium in clays. It may be carried along by alumina in colloidal suspensions," p. 719.

"The hypovanadous salts are among the most powerful reducing agents in chemistry. The neutral and acidic solutions absorb oxygen very energetically; they decompose water; and rapidly bleach litmus, indigo blue, and other vegetable colours. The hypovanadous hydroxide which is precipitated by alkali-lye begins immediately to decompose the water with the evolution of hydrogen and the formation of vanadous hydroxide, (VOH_3). According to Piccini and Marino, when the solution of a hypovanadous salt is treated with sodium carbonate, it gives a violet precipitate which decomposes at once. Sodium sulphide gives a violet precipitate which decomposes with evolution of hydrogen and hydrogen sulphide. With potassium nitrate and hydrochloric acid, there is an evolution of nitric oxide. From salts of tin, silver, gold, and platinum, the metal is precipitated by a solution of a vanadous salt; in the same way, copper is deposited quantitatively from its solution. It is worthy of note that chromous salts reduce cupric salts only to cuprous oxide," p. 740.

"Tantalum can be used as cathode in electrolytic analysis, etc.; thus, according to C. W. Balke, it can be used for the deposition of zinc since it does not alloy with the metal, and, if used for the electrodisposition of gold and silver these metals can be dissolved from the cathode with aqua regia which does not attack tantalum," p. 893.

"According to Morgenroth and Rosenthal, potassium hexatantalate does not kill the trypanosomes of mice, though it seems to inhibit their transmission from one form to another, and it also inhibits the poisonous action of antimony compounds on the trypanosomes of mice and on mice themselves," p. 902.

Wilder D. Bancroft

The Pyrolysis of Carbon Compounds. *By Charles Dewitt Hurd. 23 × 17 cm; pp. 807. New York: Chemical Catalog Company, 1929. Price: $12.50.* "The transformation of a compound into another substance, or into other substances, through the agency of heat alone is called pyrolysis. Frequently pyrolyses are thermal decompositions, but the term 'Pyrolysis' is somewhat broader than 'Thermal Decomposition.' Also, it is more concise. In 'decompositions' there is always the implication of the formation of at least two simpler substances. In pyrolyses, this is not always the case. For example, rearrangements may be caused by heat alone. Furthermore, the formation of large molecules from small ones is often effected by heat. Both of these changes are pyrolytic ones, but it would be awkward to classify them as decompositiors," p. 9.

The chapters are entitled: pyrolysis; generalizations; aliphatic hydrocarbons; cyclic hydrocarbons; petroleum, rubber, and related hydrocarbons; halogen compounds and inorganic esters; alcohols and phenols; ethers; peroxides; aldehydes; ammono-aldehydes, and ketones; carbohydrates, wood, and coal; amines; acids; dibasic acids; hydroxy-acids and amino-acids; salts of organic acids; esters; acid chlorides and acid anhydrides; amides, anilides, hydrazides, cyanides; urea, isocyanates, and related compounds; hydrazines and related substances; *nitro compounds, hydroylamine and related substances, rearrangements* of the Beckmann, Lossen, Hofmann, and Curtius types; N-heterocyclic compounds; sulfur compounds; the pyrolysis of organic compounds of other inorganic elements; polymerizations and depolymerizations."

The book contains an enormous collection of facts and is valuable on that account. The theoretical treatment is in rather a rudimentary stage. The author is not willing to say that the weakest bond breaks first and that you find out which is the weakest bond by seeing which breaks first. That would be too obvious. It sounds much better to say that "in the pyrolysis of a hydrocarbon, there is a tendency to produce radicals of low electron attraction," p. 28.

"If hexane is heated for a short time at 600°, it decomposes chiefly into methane and amylene, ethylene and propylene. A much higher temperature is necessary for the liberation of hydrogen. At 1200° hexane decomposes largely into carbon and hydrogen. . . . Benzene is far more resistant to heat than is hexane. When benzene is broken down, however, hydrogen is eliminated and diphenyl is formed," p. 15.

"The thermal decomposition of methane by an incandescent wire (platinum bands, 0.01 mm. *thick, coated with a mixture of* $CaO : BaF_2 = 1:10$*) is strictly monomolecular*. . . . Only the methane molecules which collide with the wire are decomposed," p. 51. "The work of Staudinger lends some support to the view that butadiene is the essential intermediate in the formation of aromatics. . . . The influence of heat and high pressure on ethylene is quite different from that of heat alone. Under a pressure of 70 atmospheres, ethylene begins to polymerize at 325°, and at 380°-400° the polymerization is so rapid that there is a diminution in pressure of five atmospheres per minute. At the conclusion of this pressure change, the pressure (after cooling) is but 25-30 atmospheres. . . . Without pressure there is no such polymerization, regardless of the temperature," p. 60.

Rittman, Byron and Egloff reach the conclusion the course of the cracking reaction in the aromatic series may be indicated as follows, and that any reverse reaction is negligible: higher benzene homologues → lower benzene homologues → benzene → diphenyl → naphthalene, anthracene → carbon and gas. "Such a statement as this needs interpretation since it has been shown that pure benzene or pure diphenyl or pure anthracene behaves differently. It is not questioned that higher benzene homologues tend to yield benzene in large measure; but the very fact that these homologues have produced the benzene is sufficient indication that gaseous olefines such as ethylene or butadiene are present, and that these are the responsible factors in the synthesis of naphthalene or anthracene. *Diphenyl* is formed from benzene; but it plays little or no part in the production of naphthalene or of anthracene," p. 105.

"Without attempting to give a detailed account of the development of the structure of the rubber hydrocarbon, Staudinger's formula, a huge continuous-chain molecule of indefinite size, appears to be most in accord with present data. Very probably, the chain of carbon atoms is twisted, so that certain carbon atoms represented as being far distant from others are actually close to them," p. 119.

"The rearrangement of an alkyl bromide when heated may be considered as taking place in two steps; first, the bromide dissociates into hydrogen bromide and alkylene, and second, the products recombine to form the isomeric alkyl bromide. The bromide goes to the more positive carbon atom, which in accordance with the idea of electron displacement is the one to which the most alkyl groups are attached," p. 127.

"The non-catalytic decomposition of purified nitrocellulose at 25° is practically negligible; its period of half-life is 7000 years. As the substance is purified, the rate of decomposition sinks to a minimum value for a given degree of nitration. Much the same effect is noted in the case of nitroglycerine. Here the rate of decomposition is a function of the temperature, and between 95°-125° it doubles for a rise of 5°. The nitrogen is disengaged wholly as NO_2. This is in contrast to the behavior of guncotton, from which only 40 percent of nitrogen is evolved as NO_2 at 135°. Nitroglycerin has a higher rate of decomposition than guncotton under similar conditions," p. 146.

Ethylene oxide rearranges into acetaldehyde at 400°-420° and this rearrangement occurs at 200° in the presence of alumina. Mlle. Peytral has found that three reactions take place simultaneously if the vapor is passed rapidly through a hot tube, the reaction products being CH_3CHO, $4HCHO + C_4H_8$, and $C_2H_2 + H_2O$. The decomposition is an exothermic one, the temperature of the gas rising in 0.002 seconds from 571° to 1200°, p. 181.

"Fichter favors the mechanism originally proposed by Schall [for the Kolbe synthesis], which states that the acid peroxides are first formed at the anode; hydrocarbons then come by the decomposition of these peroxides:

$$R.CO_2.CO_2.R \rightarrow R.R. + 2CO_2.$$

Walker, however, opposes this view, and cites the fact that methane is always a product of pyrolysis but is never found in the anode gases.

"By heating succinyl peroxide in a bomb at 180° (some air present), the volume relationships of the gaseous products are as follows: carbon dioxide, 55 percent; ethylene, 21 percent; methane, 6.9 percent; carbon monoxide, 6.5 percent; nitrogen, 9.7 percent; and oxygen, 0.6 percent. The instability of succinyl peroxide above 110° has also been noted by Gilman and Adams. A mixed peroxide, acetylperoxide succinic acid, if heated in a bomb at 180° for ten minutes, gives a 94 percent yield of *n*-butyric acid,

$$CH_3CO.O.O.CO.CH_2CH_2CO_2H \rightarrow 2CO_2 + CH_3CH_2CH_2CO_2H.$$

This, again, is confirmatory evidence for the intermediate formation of peroxides in Kolbe's electrochemical synthesis of hydrocarbons, since it is similar to the electrochemical synthesis of ethyl butyrate from a mixture of potassium acetate and potassium ethyl succinate. Evidence against the formation of free radicals in Kolbe's synthesis was furnished by Erlenmeyer. He found that only traces of methyl bromide or of methyl iodide are formed when a forty percent potassium acetate solution is electrolyzed in the presence of bromine or iodine," p. 233. Fichter and Erlenmeyer demonstrated "the absence of methyl iodide when diacetyl peroxide and iodine are exploded together. These experiments show that the radicals *methyl* or *phenyl* do not become free, but remain in their sphere of attraction," p. 233.

"It has recently been demonstrated [by Hinshelwood] that the thermal decomposition of gaseous acetaldehyde between 430° and 592° is homogeneous and bimolecular," p. 237. "Benzaldehyde is the only simple aromatic aldehyde that has been studied extensively. Its mode of decomposition varies decidedly with the circumstances. In the vapor phase, at sufficiently high temperatures the simple decomposition into carbon monoxide and benzene is almost the exclusive primary reaction. With a sealed-tube reaction at about 350°, the change is almost exclusively in the direction of the Cannizzaro reaction, giving benzyl benzoate. Metallic catalysts, such as reduced nickel, appear to assist the elimination of carbon monoxide from aldehydes; with benzaldehyde the conversion into pure carbom monoxide and benzene takes place at 220°, and with furfural at 270°. The condensation of aldehydes to esters is especially catalysed by aluminum ethoxide, particularly in the presence of zinc chloride as a promotor. This is the Tischtschenko reaction," p. 239.

"The pyrogenic decomposition of acetone into ketene is by far the best synthetic method for ketene. Because of the value of ketene as an acetylating agent, the optimum conditions for ketene production have been determined.... For practical purposes, the following conditions appear to be best: temperature, 700°; rate of flow of acetone, 5 cc. per minute; decomposition of acetone, between 25-40 percent of that introduced. These conditions give consistent yields of ketene which range between 35-45 percent, some three or four times better than the yield originally reported by Schmidlin and Bergman," p. 249. "No catalysts have been produced as yet for ketene production from acetone. At 270°, over nickel, acetone is decomposed rapidly into methane, carbon monoxide, hydrogen, and carbon. Copper has no effect on ketones, at least below 400°," p. 251.

"One of the first effects of heat on starch is a conversion into dextrin, a process which is undoubtedly started by the flatiron whenever starched goods are ironed. The fact that dextrins are more readily water-soluble than starches becomes, therefore, a point of more than passing interest insofar as laundries are concerned," p. 276. Almost no methanol is produced by the pyrolysis of cellulose, and all evidence seems to indicate lignin as the source of the wood alcohol," p. 284. "In the light of their work [Howard and Derick], it seems established that the mechanism of the Hofmann rearrangement requires a preliminary dissociation of methyl (or alkyl) chloride from methylaniline hydrochloride and subsequent addition to a second molecule until trimethylphenylammonium chloride is formed, amd that this is the compound which rearranges," p. 323. "Ammonia is a dehalogenating agent for organic chlorides at high temperatures (700°-800°). In many cases, the halogen is eliminated quantitatively as ammonium chloride, but with some aromatic halides, there results only seventy percent of the theoretical amount," p. 324.

"Shaw and Sebrell reported that abietic acid gives no water on heating, but that it is readily oxidized to a monoxy derivative (even in a current of commercial carbon dioxide gas which invariably contains a little oxygen). It is this monoxy derivative which readily evolves water on heating at 180° to produce monoxyabietic anhydride. If abietic acid is heated in a current of *pure* carbon dioxide, no water is eliminated," p. 347. "It was Blaise who pointed out that aldehydes could be prepared in good yields by the distillation of lactides, and it is reasonable to infer that the loss of carbon monoxide [on heating α-hydroxy acids] is more properly a function of the lactide than of the α-hydroxy acid," p. 426.

"Normally, formic acid pyrolyzes only into $H_2 + CO_2$, or into $H_2O + CO$; but when its vapors are passed over zinc oxide, considerable amounts of methanol and formaldehyde result. Thoria behaves similarly," p. 479. "The yield of acetone from various acetates is influenced profoundly by the metallic part of the molecule. According to Rojahn and Schulten, dry distillation of lithium acetate leads to a 93 percent yield of acetone as compared with a 50 percent yield from sodium acetate," p. 482. "Werner has demonstrated that urea is not a 'carbamide,' and that urea formation must invariably be preceded by the formation of *iso*cyanic acid," p. 513.

"One is accustomed to think of the formation of acetic anhydride in terms of "sodium acetate + acetyl chloride," or of "sodium acetate + chlorides of sulfur or phosphorus"; but, at present, perhaps the cheapest method for its manufacture is from *ethylidene diacetate:*

$$CH_3CH(OCOCH_3)_2 \longrightarrow CH_3CHO + (CH_3CO)_2O.$$

The raw materials for the preparation of this substance are acetylene, air, and catalysts. Essentially, its decomposition is one that is a thermal decomposition, but in practice, catalysts (acids, zinc chloride, sulfur dioxide and trioxide, etc.) are usually inserted to effect the transformation at a fairly low temperature," p. 534.

"Usually, one is accustomed to regard azo dyes as being fast to ironing; but blue and violet benzidine dyes become corinth-red when touched with a hot iron. This is probably a colloidal effect, however, rather than a pyrolytic one. It confirms the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the fiber blue and the smaller corinth-red. Thus, heat increases the degree of dispersion. Since the red color may also be formed, although more imperfectly, by desiccation over sulfuric acid, the color changes may thus be connected with dehydration and simultaneous increase in the degree of dispersion," p. 640.

"Tetraethyl lead decomposes by boiling. It can be distilled in a vacuum, however, or distilled in steam. This compound, so well known at present as an anti-knock material, undergoes a monomolecular decomposition to give fine particles of free lead. This fact has been utilized in the development of theories to explain the anti-knock activity. Since a lead sol in gasoline has the same activity as a solution of lead tetraethyl, this supports the idea that lead tetraethyl functions by its thermal decomposition ahead of the flame with the formation of pyrophoric particles, which then form centers for the propagation of the combustion. The same is true of iron sols and nickel sols, which have the same anti-knock activity as iron carbonyl or nickel carbonyl," p. 729.

Two apparently contradictory statements on the polymerization of isoprene are made by Weil and by Schotz respectively, p. 736. "It need only be said that the Hofmann heat polymerization and sodium polymerization brought out by Harries and by Matthews and Strange, and the Badische polymerization, using sodium and carbon dioxide, have been used for the manufacture of synthetic rubber. Of all these processes, however, only the heat polymerization was commercially successful. During the war synthetic rubber was made by this process on a large scale, that is, to the extent of about 150 tons per month, the total production being about 2350 tons. The only other product was a small amount made by the Badische Company, by its process" (Weil). "A review of the methods of polymerization can only lead to one conclusion, namely, that polymerization with the aid of metallic sodium and similar catalytic methods are the only ones of practical importance, because all others take such a long time and in consequence demand so much plant and space as to prove very troublesome in practice." (Schotz).

The author does use the semicolon occasionally; but he is far from being an expert with it.

Wilder D. Bancroft

Theoretical and Experimental Physical Chemistry. *By J. C. Crocker and Frank Matthews. 25 × 16 cm; pp. viii + 582. New York: The Macmillan Company, 1928. Price: $6.00.* "This book is the result of some twenty-five years' experience in teaching physical chemistry. The authors have always found some difficulty in recommending a book for the Honours Degree Examinations; and this publication is an endeavour to include, in one volume, what is usually derived by the student from several sources," p. v. In this country our students do not read officially for examinations, whatever they may do actually. They read, nominally at least, because they wish to learn about the subject and consequently they should wish a different book from this. It is interesting, however, to read a book which is written avowedly with reference to examinations. It is not necessary in a book of this sort that any one chapter should come before any other particular one, so long as all the information is included. The order of presentation is therefore quite haphazard.

Part I deals with gases, the chapters being: the gas laws; the kinetic theory of gases; vaporisation and liquefaction; the continuity of the liquid and gaseous states, and van der Waals' equation. Part II takes up spectrometry with chapters headed: the spectrometer and the emission spectra of the elements; Tesla luminescence spectra; X-ray spectra and the structure of solids; the absorption of light and absorption spectra. Constitution and physical properties are the subject of Part III, the sub-heads being: volume, surface tension, and viscosity; refractivity and rotation of polarized light; the dielectric constant. Chemical energetics is discussed in Part IV under the headings: thermochemistry; the first and second laws of thermodynamics; entropy, free energy and equilibrium; the relation between internal energy and free energy. Part V deals with heterogeneous equilibrium, with two chapters entitled dissociation and fusion, and the phase rule. In Part VI under solutions and disperse systems we find three chapters: osmotic pressure; the molecular weights of substances in solution; colloids. Part VII is given up to electrochemistry with six subheads: the theory of electrolytic dissociation in solution; the motions of the ions; the conductivity of electrolytes in solution; electrolytic equilibrium in aqueous solution; electrolytic equilibrium in non-aqueous solutions; electromotive force. Chemical kinetics and reactivity are discussed in part VIII, the chapters being entitled: velocity of reaction and reactivity in homogeneous systems; influences affecting the specific velocity of reaction; photochemistry. Part IX deals with the theory of the atoms and the sub-heads are: the classification of the elements; radioactivity and the constitution of the atom; the quantum hypothesis.

There are a great many interesting things in the book. Crystalline, monohydrated potassium oxalate has a vapor pressure less than half the pressure due to chloral hydrate vapor and does not lose water when out in contact with chloral hydrate vapor at that temperature. Consequently the chloral hydrate vapor must be practically completely dissociated, a conclusion which is in accord with the vapor density, p. 20.

It was new to the reviewer that "boiling takes place with phenomenal ease and regularity in rubber vessels," p. 31. The reviewer was glad to see a paragraph, p. 53, devoted to Mme. Meyer's suggestion that one might apply a special correcting term to the temperature in the equation of state. On p. 54 is a clear paragraph on the parachor. "A more recent development is the work of Sugden on *parachors*. Here the molecular volumes of different liquids are compared, virtually, under the condition of equality of surface tension, and therefore, presumably, of equal internal pressures. As these pressures are relatively large, and probably of the order of a thousand atmospheres, the importance of this condition will be readily realized."

"A point of interest arose in connection with the fluorescence spectrum of benzene in alcoholic solution. Hartley had found that when benzene passes from the state of vapour to that of solution, the absorption bands were shifted towards the red end by about 10 to 20 Ångström units. Similarly, McVicker, Marsh and Stewart show that if 19 units are added to the frequencies of the benzene fluorescence bands, previously determined by Dickson, the positions of the lines are practically identical with those of the brightest lines of the Telsa luminescence spectrum.

"The inference is drawn that the fluorescence spectrum and the Tesla spectrum have a common origin. Another interesting fact was elucidated by the comparison of the absorption spectrum of benzene vapour, previously determined by Hartley, with the Tesla luminescence spectrum. In all cases where the bands are in evidence in both spectra, within the limits of error, the positions are practically identical. So that, apparently, the absorption spectrum is simply the *reversed* Tesla luminescence spectrum. These results were confirmed by later work on benzene vapour at a lower pressure. Under a pressure of 1.6 mm. two further groups of bands at the ultra-violet end were developed. They were dissimilar in type to the previous bands, being less sharply defined, and of much smaller intensity. The spacing was also different. The sharpest bands of the series, however, again corresponded exactly to a series of absorption bands in benzene vapour, determined by Henri.

"It would appear, therefore, that the Tesla luminescence spectrum, the absorption spectrum, and the fluorescence spectrum of benzene, are due to a common cause," p. 71.

When discussing the X-ray spectrum of potassium chloride, p. 80, the statement is made that it is not the molecule which is responsible for the spectrum but the atoms. No reference is made to ions, so one cannot be sure that this wording indicates a new point of view; but it is at least suggestive.

"On comparing the absorption spectra of acetyl acetone and its metallic derivatives, Baly found that the absorption band in the spectrum of a metallic derivative was always nearer to the red end of the spectrum than was the band for acetyl acetone itself; and this he found to be generally true. So that, just as increase of atomic weight in the alkali group of metals displaces analogous spectral lines towards the red end of the spectrum; so does increase of molecular weight, in the case of tautomeric substances, similarly displace the absorption band.

"By the refractometric method Brühl has shown that apparently the sodium derivatives of these tautomeric substances consist purely of the enolic forms, whereas the ultra-violet absorption spectra indicate that both enolic and ketonic forms are present. It has been suggested by Baly, therefore, that possibly ultra-violet light has a ketonising tendency. It hardly seems likely, however, that ketonisation would be effected in an appreciable degree by ultra-violet light during the relatively short exposure necessary for a photograph," p. 85.

"Hartley pointed out the enormous absorption of *tri-phenyl-methane* for ultra-violet light, which is far in excess of the absorbing power of benzene; and this has led to the view that the extraordinary absorptive power of dyes of the tri-phenyl-methane type can be satisfactorily explained by the displacement of the tri-phenyl-methane absorption bands into the visible spectrum, owing to the 'weighting' effect of the substitutent groups in the molecule of the dye. Further, it has been suggested that the absorption bands in the two cases are analogous, and that there is no essential difference in character between the ultra-violet absorption spectrum of *tri-phenyl-methane* and the visible spectra of *rosaniline* and its salts," p. 92.

"In most cases the solvent exerts an influence on the rotation of the dissolved substance, and thus its specific rotation varies in different solvents, and is different, in solution, from that of the pure substance. The specific rotation varies also with the concentration of the solution. The effect of the solvent becomes greater with increasing dilution. In the case of dilute aqueous solutions of active salts, the specific rotation gradually changes with dilution, until at infinite dilution a limiting value is reached for each salt. If molecular rotations are taken, instead of specific rotations, it has been found that for all salts of the same optically-active acid, and for all salts of the same active base, the limiting molecular rotation is the same. At infinite dilution therefore the optically-active portion of each salt is in the same condition, which is in accordance with the electrolytic theory of solution. It is essential therefore that, for analytical purposes, measurements of rotation should be made under comparable conditions, and in solutions as dilute as possible. In practice, 10% is usually found to be a reasonable strength," p. 133.

On pp. 143-144 there are two excellent tables by Walden, showing the connection between dielectric constant and electrolytic dissociation. The calculation of molecular weights from the temperature coefficient of the solubility, p. 169, is distinctly interesting theoretically. One does not see, however, why the saturation solution pressure or osmotic pressure and the depression of the freezing-point of the solution should be taken up nearly eighty pages before osmotic pressure.

The reviewer welcomes the table on p. 242, giving Alder Wright's data for the dineric equilibrium between chloroform, water, and acetic acid. Most people ignore these data entirely. Plait-point is a better term than limiting-point, p. 243, for the concentration at which the upper and lower liquid phases become identical. It seems to the reviewer that it would have been better to have at least referred to the disturbing effects of surface tension, gravity, etc., on the phase rule relations, p. 215. The account of the two modifications in the melt with sulphur, p. 224, should have come on p. 228 under dynamic isomerides. It is absurd to recommend for reading on the phase rule, p. 244, the books by Rivett and by the reviewer, and not to mention Findlay's book, which is far and away the best of the three.

There is a good discussion of McBain's work on soap, p. 298, and of the hydration of the ions, p. 325. The reviewer hails with delight the table on the strengths of the weak organic bases, p. 355. He had not realized, for instance, that quinine was three thousand times as strong as o-aminobenzoic acid. There is a good account of pseudo-acids, p. 359, and the table for the migration velocities of cations in methyl alcohol, p. 369, is valuable. The reviewer had quite forgotten Donnan and LeRossignol's reaction of the fifth order, p, 456, between potassium ferricyanide and potassium iodide. The account of simultaneous reactions, p. 462, is good, though the reviewer would have preferred a reference to Wildermann (1891) rather than to Arnall (1925) if only one reference is to be given. The reviewer would have given both.

There are some things which should be changed in a later edition. Why should not the student be shown how to combine $v = KT$ and $p = k_1T$ so as to get $pv = RT$, p.3? The most obvious way of combining them gives $pv = RT^2$, which we know is not right. While it is arithmetically correct to say, p. 5, that $R = pv/T$, which "is the expression for the external work done when one gram-molecule of the gas is heated through 1°C. at constant pressure," it would be very much clearer to say that $R = pdv/dT$.

The authors play fast and loose, p. 7, with the question of the oxygen standard. "It is more convenient to deal with relative densities than with absolute densities and $O = 16$ is taken as the standard. . . . Burt and Edgar have shown, from the volumes in which oxygen and hydrogen combine, that the relative density of hydrogen is 1.0077, which is so nearly unity that for practical purposes it can usually be taken as one, and becomes a more conconvenient standard than $O = 16$."

On p. 35 is the statement that "it was discovered by Baron Cagniard de la Tour in 1822, that when a liquid was heated in a closed space, under proper conditions, the liquid became thinner in appearance and more mobile and at a certain temperature, fixed for each liquid, it volatilised and the vapour completely filled the tube." The word 'thinner' is not very descriptive; but the chief trouble is the word 'volatilise.' This should mean that the meniscus descends to the bottom of the tube and disappears there, just as it would if one actually volatilized the liquid. Actually the meniscus remains stationary, if the proportions are right, and disappears. The analogy is with the Cheshire cat and not with volatilization.

The authors adopt the German spelling, 'kathode,' p. 250. One would think that the Faraday Society would head a movement to retain Faraday's spelling; but the German influence is apparently far too strong. On p. 267 the authors give the formula $(p_o-p_1)/p_o = n/N$, which is absurd because the partial pressure of the solvent does not become zero when $n = N$. It must be said, in the authors' favor that they do emphasize the fact that N has nothing to do with the molecular weight of the solvent as liquid.

Hardy's valency rule is given, p.285, as though it were general. In the discussion on emulsions, p. 294, the authors have forgotten that there are two sides to the emulsifying film and consequently two surface tensions. They are discussing the wrong one. It is not true, p. 294, that "suspensoids are probably stabilised chiefly by adsorbed liquid." Apparently the authors read by preference books published by J. and A. Churchill, p. 301. No other hypothesis seems to fit the facts.

On p. 304 the authors say that "in the case of cobalt chloride the change of colour from pink to blue, by the action of hydrochloric acid, might be explained by the dehydration of the cobalt ion, since anhydrous cobalt salts are blue. On the other hand it would be a little difficult to apply this explanation to the copper salts. Anhydrous copper chloride is liver-coloured, and anhydrous copper sulphate is white [they mean colorless]; and further, all soluble copper salts in aqueous solutions are blue, which appears to indicate that the color-producing part of the salt, in each case, is one and the same agent, namely the copper ion itself."

There is nothing to prevent the blue being due to a hydrated copper ion or radical. In fact, the reviewer believes that the group $Cu.(H_2O)_{2+n}$ is blue and the groups $Cu.H_2O$ and $Cu.2H_2O$ are green.

On p. 312 the authors follow Ostwald—without saying so—and consider methyl orange as a relatively strong acid instead of a weak base. Nobody disputes that the sulphonic acid group is a strong acid; but this group has nothing directly to do with the color change, because we get the same color changes when there is no sulphonic acid group there. It is easy to see why Ostwald should have made this mistake originally; but one does not see at all why it should be perpetuated.

Wilder D. Bancroft

Geologie und Radioaktivität. *By Gerhard Kirsch. 24 × 16 cm; pp. vi + 214. Wien and Berlin: Julius Springer, 1928. Price: 16 marks; bound, 17.40 marks.* This book is based upon lectures given by the author in the University of Vienna in the year 1926-27. As the subtitle states, it treats the processes of radioactivity as clocks for the measurement of geological time and as sources of geo-physical energy. It is concerned primarily with the advances rendered possible by applying radioactive methods to the problems connected with the past history and chronology of the earth.

For the benefit of those not familiar with the physical side of the subject, the main phenomena and theories of radioactivity are treated in a straightforward manner in an introduction of some 30 pages, after which the book is divided into three main sections. In the first, after some account of the practical methods employed, the uranium, thorium and potassium content of the typical acidic and basic rocks is discussed and the quantities of heat these may be expected to evolve in the earth's interior. In this connection potassium is still very much a "dark horse" as its quantity—variously estimated at from 0.4 to 0.04% of the earth's crust—so greatly exceeds the others and its actual heat evolution is very doubtful

The next and perhaps most interesting and important, if also most speculative, section deals systematically with the theories of Joly, Holmes and Jeffreys as to the effects such materials may have produced on the past history and present evolution of the globe. Here the difficulty is to know how deep into the interior they extend, for if they extended to the centre,—that is if the whole earth were of the same radioactive composition as the crust we know—they would be producing many hundred times as much heat as the earth is losing by radiation. That they extend into the dense and probably metallic core is not probable, but the old view that the earth is steadily cooling still maintained by Jeffreys, leads to such a thin crust—some 10 to 20 kilometres of the same average composition as the surface—that it is regarded as contrary to the geological evidence. On the other hand, Washington's estimates of layers of granite, basalt and peridotite, respectively 20, 40 and 1500 kilometres in mean thickness, surrounding an iron core, obviously must lead to the conclusion that the interior is steadily getting hotter. This forms the starting point of the sweeping generalizations of Joly concerning magmatic cycles, developed and extended by Holmes. After the first vivid realisation of the more sensational possibilities involved in the conclusion that the earth beneath our feet is steadily getting hotter and may be expected to go up at any moment, and in the more modern spirit of geologic gradualism as opposed to the older catastrophism; Joly has based upon.this conclusion his theory of the building of mountain ranges. In brief, the periodic fusion of the underlying layers as the radioactive heat accumulates, and the floating up of the unliquefied and lighter parts as mountain ranges, is believed to be responsible for the four or five great magmatic cycles recognised in geologic history. These seem to have occurred with fair regularity every forty or fifty million years.

The last section deals with the simpler and more straightforward determination of geologic age by the lead to uranium-plus-thorium ratio, and to the less dependable methods involving the helium ratio and the evidence of pleochroic halos. Here again there appears to be abundant confirmatory evidence of periodic rearrangements of the strata forming the earth's crust, the length of the period between upheavals corresponding well with the figure just mentioned.

There is little doubt that the lead ratio, when perfected, will give something like an absolute chronometer of geological time. At present we are still perhaps far from this. It is not enough to deal with averages. All the relative data should be known for each single specimen, and this is at present far from being the case. The atomic weight of the lead, and, when that becomes possible, its isotopic constitution, require to be known, not merely its ratio to the radioactive constituents. Also there are now looming up very big questions, almost prophetically foreseen and maintained by Joly before anyone else would have entertained the possibility, that the uranium clock has *not* been keeping time, that in fact it has been running ever slower and slower through the ages. The evidence now accumulating, that the acrinium series is derived from an independent relatively shorter lived, isotope of uranium, makes this conclusion, which at first seemed so heretical, now inevitable.

Even so, the lead-ratio, if not yet a chronometer, is no bad clock. Apart from Baron de Geer's marvellous extension of the earth's chronology back to some 12,000 B. C. by following the successive moraines left each year by the receding Polar ice cap when the last glacial epoch was relaxing its grip, there has been nothing in geology so direct and unequivocal. As directly interpreted, it puts the age of some of the archaic rocks as from one to two thousand million years, but the present author is content apparently with somewhat more conservative estimates. He shows how, with greater accuracy and refinement being introduced into the method, it is possible to distinguish the same periodic difference of age between different formations of the same mineral from the same locality as have been mentioned in connection with the magmatic cycles.

Naturally this book, since so much of the work dealt with has been the contribution of British investigators, will appeal rather to the German than to the English speaking student. At least it has always seemed to the writer to be peculiarly futile to read work originally published in one's native language in some foreign tongue. But as an up-to-date and comprehensive summary, it can be generally recommended, while its comprehensive bibliography of a very scattered literature falling between two sciences alone makes it welcome. If a word of criticism is allowable, concerning the form and method of presentation of the matter, it is that there seems to be a lack of a distinct and easily followed thread throughout the narrative. The pages all look too much alike, one has to wade through almost the whole book to retrace any small point that is being looked for, and the index is not sufficiently extensive to be of much use. If the book were broken up into more short-titled sections and the main data and conclusions more progressively presented and conspicuously recapitulated, its value to the student would be greatly enhanced.

Frederick Soddy

A Laboratory Manual of Elementary Physical Chemistry. *By Edward Mack, Jr. and Wesley G. France. 22 × 14 cm; pp. xi + 195. New York: D. Van Nostrand Co., 1928. Price $2.00; 8 shillings, 6 pence.* At the present time a number of good and useful books on practical physical chemistry are available. They differ to some extent in the type of experiment described and in the complexity of the apparatus required.

In the book under review several experiments are given which are usually dealt with in the Physics Laboratory rather than in the Chemical one—such as those which deal with the ratio of specific heat of gases and thermal conductivities of gases. As a knowledge of these quantities is of considerable interest to chemists it is very useful to have their determination carefully described in a book designed for chemists. In addition to a few very physical exercises of this sort, all the usual physico-chemical methods are illustrated by well chosen and attractive experiments, the whole field being very satisfactorily covered.

A majority of the experiments given need the resources of a well-equipped laboratory and, while they are quite suitable for advanced students, there are many students of chemistry who would probably gain more from simpler exercises carried out with less elaborate apparatus.

Each experiment is accompanied by a useful theoretical introduction and numerous references to original papers and standard text books are also given. This is a very good plan.

The book is well written and well produced and it is likely to take an important place in laboratory instruction.

H. Bassett.

THE FREQUENCY DEPENDENCE OF THE ELECTRICAL CONDUCTANCE OF SOLUTIONS OF STRONG ELECTROLYTES[*]

BY HANS FALKENHAGEN[1] AND JOHN WARREN WILLIAMS[2]

I. Introduction

The interionic attraction theory of the behavior of ions in dilute solutions, based on the fact that the thickness, κ of the ionic atmosphere of mean charge surrounding each ion has to be proportional to the square root of the concentration of the solution if the principal forces between ions are the ordinary Coulomb forces, has been utilized by Debye and his students[3] to show that the square-root law, found experimentally by Kohlrausch,[4] is the correct one to explain the change in electrical conductance of dilute solutions of electrolytes with concentration. It was shown that the ionic atmosphere, built about each ion, is characterized by certain properties; for example, it has (as already mentioned) a definite thickness which is of extreme importance not only for the simple conductance theory but also for the activity theory[5] now so well known in physics and chemistry.

The ionic atmosphere possesses, in addition, a finite time of relaxation. This atmosphere can neither be destroyed nor created in an infinitely small period of time. If an ion is suddenly separated from the solution, the regularity in its neighborhood will cease to exist because it owes its presence only to the force field of the central ion. The transfer to the regular orientation, with reference to the point where the ion was, will take place gradually. The time necessary for this change is the time of relaxation, and is dependent on a number of factors. Its order of magnitude in seconds has been shown[3] to be

$$\bar{\Theta} = \frac{10^{-10}}{\gamma} \text{ sec.} \tag{1}$$

where γ is the concentration of the solution in moles per liter. The values of $\bar{\Theta}$ for $\gamma = 0.001$ in water at 18°C for several electrolytes are given in Table I. Included in this table are corresponding wave lengths whose significance will be recognized later.

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[*] Contribution from the Physikalisches Institut der Universität, Leipzig.

[1] Fellow of the International Education Board.

[2] National Research Council Fellow.

[3] Debye and Hückel: Physik. Z., **24**, 305 (1923); Onsager: **27**, 388 (1926); **28**, 277 (1927). See also Hückel: Ergeb. exakt. Naturwiss., **3**, 199 (1924); Baars: Handbuch der Physik von Geiger-Scheel, **13**, 397 (1928); Williams and Falkenhagen: Chemical Reviews, Forthcoming publication.

[4] See Kohlrausch und Holborn: "Das Leitvermögen der Elektrolyte" (1916).

[5] Debye and Hückel: Physik. Z. **24**, 185 (1923); Debye: **25**, 97 (1924).

TABLE I

Values of the Time of Relaxation, $\bar{\Theta}$·

Electrolyte	Time of Relaxation	Corresponding Wave Lengths
KCl	0.553×10^{-7} sec.	16.6 meters
HCl	$0.189 \times$ "	5.67 "
$MgCl_2$	$0.323 \times$ "	9.69 "
$CdSO_4$	$0.314 \times$ "	9.44 "
$LaCl_3$	$0.208 \times$ "	6.24 "

Recently it has been shown that as a necessary consequence of the existence of this finite time of relaxation, an electrical conductance of dilute solutions of strong electrolytes which is dependent on the frequency must result. This effect has been discussed previously by Debye and one of us,[6] and by ourselves.[7] The present paper reviews in some detail this important development; in addition a considerable amount of original material has been added.

Before proceeding with the discussion, it may be interesting to state that the effect predicted by the theory has been shown to exist by Sack[8] in preliminary measurements made in this laboratory. The experimental study of this effect is being continued both here and at the University of Wisconsin.

II. Discussion of Frequency Effect

Consider an ion, surrounded by its ionic atmosphere, to be suddenly removed from the solution. The regular distribution of the ions in the neighborhood of the ion can no longer exist, because the central force-field, which is the cause of the regular distribution, has been removed. The change of the distribution of the charges of the ionic atmosphere to a random distribution with respect to the point where the central ion was, will take place gradually. The disappearance of this equilibrium position has been given mathematically in the original articles,[6] it is sufficient for our purpose to give the result by means of a graph (Fig. 1).

For the quantity of electricity, dQ, which lies between spheres having radii, r and r + dr, the following relation holds

$$dQ = -\, y\kappa e\, dr \qquad (2)$$

where

$$y = \kappa r e^{-\kappa r}\, J(\kappa r, \tau)$$

$$J(\tau, \kappa r) = \frac{1}{2\pi}\int_{\sqrt{\tau} - \frac{\kappa r}{2\sqrt{\tau}}}^{\infty} e^{-x^2} dx$$

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[6] Debye and Falkenhagen: Physik. Z., **29**, 121 (1928).

[7] Falkenhagen and Williams: Z. physik. Chem., **A137**, 399 (1928).

[8] Sack: Physik. Z., **29**, 627 (1928).

and $$\tau = \frac{t}{\bar{\Theta}} \qquad \text{where } \bar{\Theta} = \frac{\rho_1\rho_2}{\rho_1+\rho_2}\,\frac{1}{\kappa^2 kT}$$

The quantity y is a measure for the density of the ionic atmosphere at different times and in a shell of thickness dr at different distances r from the ion in consideration. In Fig. 1 is shown y for $\tau = 0$, $\tau = 0.25$ and $\tau = 1$ as a function of κr. For each time y has a maximum value which decreases as κr is increased. Or, it may be said that the maximum of the thickness y at time $t = 0$ lies at $\kappa r = 1$, at time $t = 0.25\bar{\Theta}$ at $\kappa r \sim 1.5$ and finally at time $t = \bar{\Theta}$ at $\kappa r \sim 2$. The maxima themselves for these times are given approximately by the numbers 0.36, 0.31, and 0.14. Fig. 1 shows how the density in the ionic atmosphere at the time $4\bar{\Theta}$ is small compared to the original density at time zero. After the four-fold time of relaxation, $4\bar{\Theta}$, the density has already disappeared. The time of relaxation $\bar{\Theta}$ is, therefore, a measure for the disappearance of the equilibrium condition. It has already been shown[6,7] that it is of the order of magnitude $\frac{10^{-10}}{\gamma}$ sec. In the treatment to follow it is useful to introduce the time of relaxation Θ which is defined by the relation

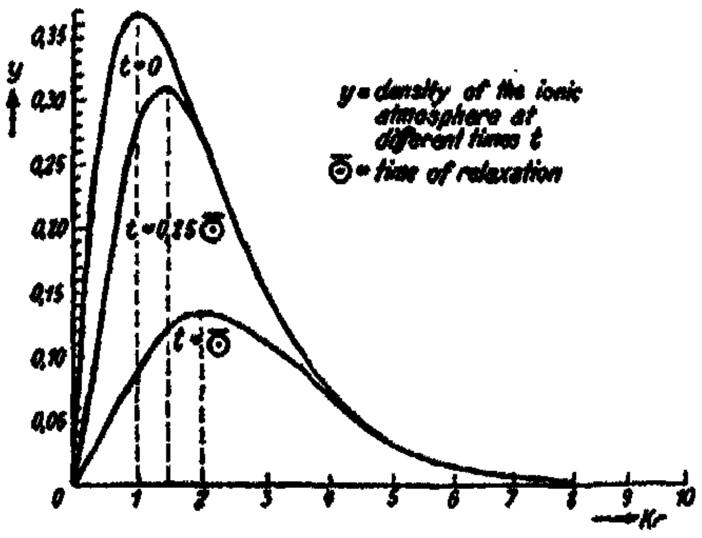

FIG. 1

$$\Theta = \frac{\bar{\Theta}}{q}, \text{ where q is given by the equation} \tag{3}$$

$$q = \frac{\bar{L}_1 z_2 + \bar{L}_2 z_1}{(z_1 + z_2)\,\bar{L}_1 z_2^2 + \bar{L}_2 z_1^2} \cdot z_1 z_2 \tag{3a}$$

where $\bar{L}_1$ and L_2 are the mobilities of ions 1 and 2, and z_1 and z_2 are their valences (See Reference 3). It is of course evident that either time of relaxation could be used in any discussion of this sort.*

The reason why a dispersion of the electrical conductance must exist may be shown in the following manner. If an ion is in motion due to the action of an external electrical field, there will be a density of charge which is too small before and too large behind any ion upon which attention is fixed. Therefore, there will be a dissymmetry of the ionic atmosphere which becomes

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* For a detailed consideration of these two times of relaxation see Reference 7.

more and more important the greater the average velocity of the ion is. The result is a resisting force which has been called the electrical force of relaxation.[3] This electrical force of relaxation appears in the calculation as a decrease in the mobility of the ion.

It must be emphasized that the calculation of the dissymmetry can give an approximation only for small ionic velocities. In the usual cases an approximation is sufficient, but the case is different when one, as has been done by Wien[9]* in his recent experiments, causes the existence of abnormally large ionic velocities by great field strengths. The order of magnitude of the velocities in the Wien experiment was 1 meter per second contrasted to the usual velocities of the order of magnitude, 0.01 mm/sec. It can be readily shown that ions which have these high velocities will travel many times the thicknesses of their ionic atmospheres in the time of relaxation. Under these conditions, then, the ionic atmosphere can hardly be built. Therefore, in very strong fields the force which has been termed[3] the additional electrical force of relaxation is of little or no consequence, and the conductance will approach that value found at infinite dilution. This deviation from Ohm's law is exactly the effect discovered experimentally by Wien and explained in a more or less quantitative manner by Joos and Blumentritt.[10] The Wien Effect is illustrated by Fig. 2 in which the values of the field strength, X, are plotted as abscissae against values of the function $\frac{\Lambda_\infty - \Lambda_X}{\Lambda_\infty - \Lambda_{X=0}}$ as ordinates.*

If now, the experiments of Wien can be understood in the way which has been given, then the existence of the effect which is to engage our attention in this section is to be suspected. If it be assumed that an outer electrical field of oscillation frequency ω acts on the ions in the solution, then apart from their Brownian movements there is imparted to the ions a back and forth (periodic) movement. If the frequency of the field is small, the ionic atmosphere will have in each moment a dissymmetry of distribution of charges which corresponds to the momentary velocity of the ion. In other words the additional electrical force of relaxation will be the same for small frequencies of the outer field as it was for the stationary case. In the other extreme case, where the frequency of the field is extraordinarily great compared to $1/\Theta$, the situation must be different. Fixing our attention on an ion in motion, under these conditions it may be shown that[6,7] the dissymmetry of the ionic atmosphere cannot be built. This shows that if the frequency is great enough, the electrical force of relaxation disappears. Since the electrical force of relaxation is a force, which in the case of the frequencies ordi-

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[9] Wien Ann. Physik, 83, 327 (1927); Physik. Z., 28, 834 (1927). See also Reference 7.

* The discussion of the Wien experiments does not rightfully belong in an article on this subject. It is introduced at this point to assist the reasoning which leads to the explanation of the dispersion effect.

[10] Joos and Blumentritt: Physik. Z., 28, 836 (1927).

* Professor Wien has very kindly sent us the results of his most recent experiments which are in good agreement with the requirements of the theory.

narily used for the measurement of conductance, operates to resist the passage of an ion, it is evident that an increase in the conductance will appear when such frequencies are used that this force disappears. In other words, a dispersion of conductance must exist.

In this article only the results of the calculations for the general case of an unsymmetrical electrolyte, taking into consideration the Brownian movement of the ions, will be presented. Further, a discussion of a number of factors which influence the phenomenon of the dispersion will be given.

The molecular conductance, $\bar{\Lambda}$ as a function of the frequency may now be written

$$\bar{\Lambda} = \bar{\Lambda}_\infty - \bar{\Lambda}_{I\omega} - \bar{\Lambda}_{II} \tag{4}$$

where $\bar{\Lambda}_\infty$ = equivalent conductance at infinite dilution.

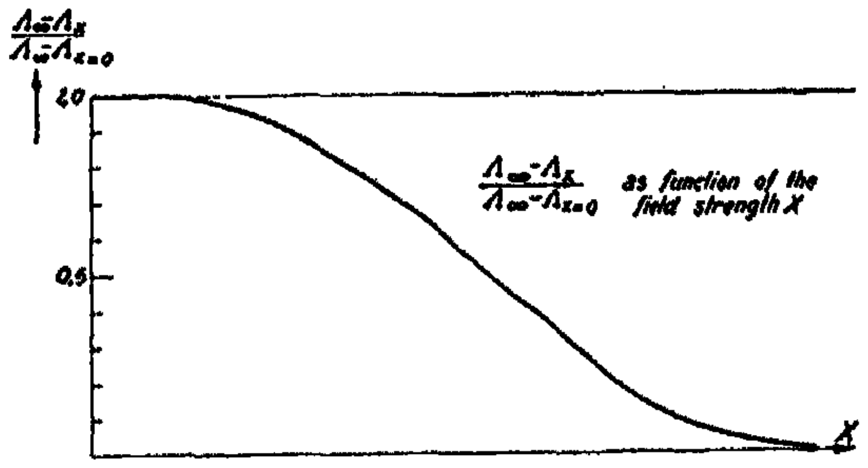

FIG. 2

$$\bar{\Lambda}_{I\omega} = \frac{|e_1e_2|}{3DkT}\kappa\bar{\Lambda}_\infty\,\bar{X}(\omega\Theta,q) \quad = \tag{4a}$$

electrical force of relaxation for frequency ω, expressed as conductance.

$$\bar{\Lambda}_{II} = \Sigma\,\frac{n_ie_i^2\kappa}{6\pi\eta}\,\frac{1000}{\gamma}\,\frac{1}{9\times 10^{11}}\,\kappa \quad = \tag{4b}$$

ordinary force due to electrophoresis (See reference 3), expressed as conductance.

Further,
$$\bar{X} = \frac{\sqrt{q}}{(1 - 1/q)^2 + \omega^2\Theta^2}\left[(1 - 1/q)\left(\bar{R} - \frac{1}{\sqrt{q}}\right) + \omega\,\Theta\,\bar{Q}\right]$$

$$\bar{R} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\Theta^2} + 1}$$

$$\bar{Q} = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + \omega^2\Theta^2} - 1}$$

D = dielectric constant of the solvent.
k = Boltzmann's constant = 1.372×10^{-16} erg/degree.
T = absolute temperature.
n_i = Number of ions of the i^{th} kind in 1 cc.
η = internal friction constant of the liquid.
e_i = charge on ion of the i^{th} kind.
γ = concentration in moles per liter of solution.

The dependence on frequency appears in the term X which is in turn dependent on $\omega\,\Theta$ and q. A knowledge of the time of relaxation is also necessary for the dispersion effect. In the case of zero frequency the expression for the molecular conductance goes over to that of the original conductance theory.[3] It is thereby assumed that the electrophoretic part of the conductance is independent of the frequency.

In order to recognize the effect of frequency most clearly, it is desirable to examine the ratio $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$. The following method serves for the calculation of the dispersion effect for any simple electrolyte, provided solvent, temperature, electrolyte, and concentration are given. The valencies z_i and mobilities $\bar{L}_i$ must also be known. According to the formulae

$$q = \frac{\bar{L}_1 z_2 + \bar{L}_2 z_1}{(z_1 + z_2)\,(\bar{L}_1 z_2^2 + \bar{L}_2 z_1^2)} \cdot z_1 z_2 \qquad (3a)$$

$$\Theta = \frac{z_1^2 z_2^2}{z_2^2 L_1 + z_1^2 L_2} \cdot \frac{15.3 \times 10^{-8}}{kT\,q\,\kappa^2} \qquad (5)$$

$$\kappa^2 = \frac{4\pi}{DkT}\,\frac{e^2 N}{1000}\,\gamma\,\Sigma\,\nu_i z_i^2 \qquad (6)$$

For water at 18°C

$$\kappa^2 = 0.05342 \times 10^{16}\,\gamma\,\Sigma\,\nu_i z_i^2 \qquad (6a)$$

at 25°C

$$\kappa^2 = 0.05385 \times 10^{16}\,\gamma\,\Sigma\,\nu_i z_i^2 \qquad (6b)$$

q, κ^2, and Θ are determined. The quantity $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ depends only on q and $\omega\Theta$. In Table II is given an interpolation table which is extremely useful; it contains values for the quantity $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ as a function of $\omega\Theta$ for five different values of q. The molecular lowering of the conductance due to the electrical force of relaxation for the stationary case $\bar{\Lambda}_{I_0}$, and the lowering due to the electrophoretic effect, $\bar{\Lambda}_{II}$ are calculated by means of the formulae

$$\bar{\Lambda}_{I_0} = \frac{|e_1 e_2|}{3DkT}\,\kappa\,\bar{\Lambda}_\infty\,\frac{q}{1 + \sqrt{q}} \qquad (4a')$$

$$\bar{\Lambda}_{II} = \frac{n_1 e_1^2 + n_2 e_2^2}{6\pi\eta}\,\frac{1000}{\gamma}\,\frac{1}{9 \times 10^{11}}\,\kappa \qquad (4b)$$

III. The Influence of Various Factors upon the Ratio $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$

The influence of concentration, mobility of the ions, dielectric constant, temperature and the valence upon the function $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ will now be discussed. The values of the valences, mobilities, and the temperature used in these sections are given in Table III. The electrolytes are HCl, LiCl, KCl, $MgCl_2$, $CdSO_4$, $LaCl_3$, $K_4Fe(CN)_6$, and $Ca_2Fe(CN)_6$.

According to this table values for the mobilities are used which agree with the best values given in the literature to within 1%; they are, therefore, sufficiently exact to be used to illustrate the effect of dispersion. The value

TABLE II*

Interpolation Table—Values of $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$

$\omega\Theta$	q = 0.5	q = 0.45	q = 0.40	q = 0.35	q = 0.30
0	1.00	1.00	1.00	1.00	1.00
0.1	0.999	0.999	0.999	0.999	0.999
0.2	0.997	0.997	0.997	0.997	0.997
0.35	0.989	0.990	0.990	0.990	0.990
0.5	0.980	0.981	0.981	0.981	0.981
0.75	0.956	0.959	0.962	0.965	0.968
1	0.930	0.934	0.938	0.942	0.946
1.25	0.904	0.909	0.913	0.918	0.922
1.5	0.876	0.882	0.888	0.894	0.900
2	0.826	0.833	0.841	0.848	0.856
2.5	0.783	0.791	0.799	0.808	0.817
3	0.745	0.753	0.763	0.773	0.785
4	0.682	0.691	0.701	0.713	0.727
6	0.593	0.603	0.614	0.628	0.643
8	0.531	0.540	0.553	0.565	0.582
10	0.486	0.496	0.507	0.520	0.537
15	0.409	0.417	0.428	0.442	0.458
20	0.360	0.368	0.378	0.390	0.406
25	0.326	0.334	0.344	0.354	0.369
30	0.299	0.307	0.317	0.327	0.342
35	0.279	0.286	0.295	0.305	0.318
40	0.261	0.267	0.277	0.287	0.299
45	0.247	0.254	0.263	0.272	0.288
50	0.235	0.242	0.250	0.259	0.271
75	0.193	0.199	0.206	0.214	0.223
100	0.168	0.173	0.179	0.186	0.195
150	0.138	0.142	0.147	0.153	0.160
200	0.1195	0.1232	0.1278	0.1328	0.1394
300	0.0983	0.1011	0.1046	0.1088	0.1145
500	0.0759	0.0783	0.0812	0.0844	0.0888
700	0.0643	0.0663	0.0688	0.07165	0.0751
1000	0.0538	0.0555	0.0576	0.0599	0.0629
5000	0.0241	0.0249	0.0258	0.0269	0.0282
10000	0.01706	0.01755	0.01824	0.0190	0.0199

* The values given in this table are accurate to within 1%.

of the molecular conductance at infinite dilution for $K_4Fe(CN)_6$ is taken from an article by Burrows.[11] At temperature 25°C this investigator gives the value 680. If the mobility of the K^+ ion at 25°C is 75, then that for the $Fe(CN)_6^{----}$ is 380. In Table IV the characteristic quantities κ^2, q, and $\Theta\gamma$ are given. The values for the thickness of the ionic atmosphere $1/\kappa$ for different concentrations may also be taken from this table.

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[11] Burrows: J. Chem. Soc., **123**, 2026 (1923).

TABLE III

Mobilities of Certain Ions

Ion	z_i	$\bar{L}_i$	t°C
H	1	315	18
K	1	65	18
Cl	1	65	18
Li	1	33	18
Mg	2	92	18
SO_4	2	136.6	18
Cd	2	92	18
Ca	2	120	25
La	3	150	18
$Fe(CN)_6$	4	380	25

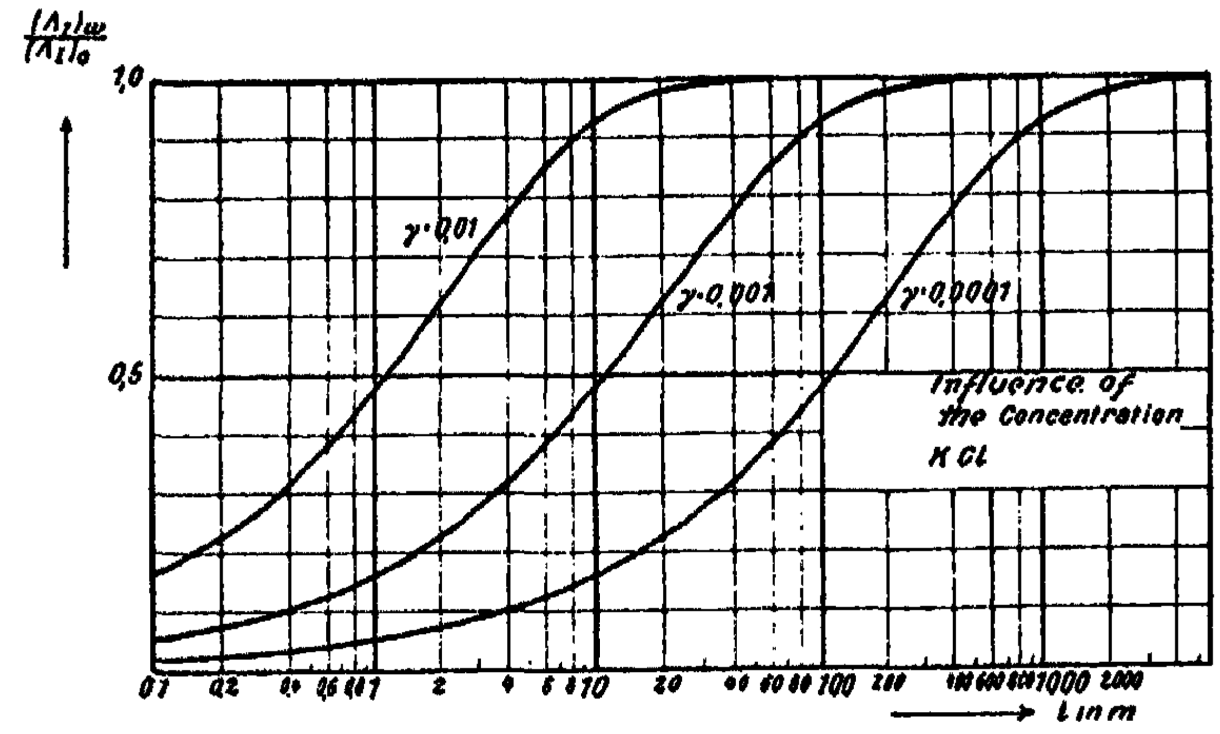

FIG. 3

TABLE IV

Values of κ^2, q and Θ

Electrolyte	$\frac{1}{\kappa} \cdot 10^{8} \sqrt{\gamma}$	κ^2	q	$\Theta\gamma$
HCl	3.06	$0.107 \times 10^{16}\gamma$	0.5	0.189×10^{-10}
KCl	3.06	.107 "	0.5	.553 "
LiCl	3.06	.107 "	0.5	.732 "
$MgCl_2$	1.77	.321 "	0.421	.323 "
$CdSO_4$	1.53	.428 "	0.5	.314 "
$LaCl_3$	1.25	.642 "	0.352	.208 "
$K_4Fe(CN)_6$	0.96	1.08 "	0.344	.102 "
$Ca_2Fe(CN)_6$	0.88	1.29 "	0.480	.113 "

Influence of the Concentration on the Dispersion of Electrical Conductance

For the purpose of the study of the effect of concentration solutions of KCl in water at 18°C will be considered. (Dielectric Constant of the solvent = 81.3). According to Table IV for concentrations $\gamma = 0.01$, $\gamma = 0.001$, and $\gamma = 0.0001$ the corresponding times of relaxation are $\Theta = 0.553 \times 10^{-8}$ sec., $\Theta = 0.553 \times 10^{-7}$ sec., and $\Theta = 0.553 \times 10^{-6}$ sec. According to Table IV the values of κ^2 are, respectively, $\kappa^2 = 0.107 \times 10^{-14}$, $\kappa^2 = 0.107 \times 10^{-13}$, and $\kappa^2 = 0.107 \times 10^{-12}$. As KCl is a symmetrical electrolyte $q = 0.5$. Therefore, by means of the interpolation table values of $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{I_0}$ as a function of $\omega\Theta$ may be written. Fig. 3, in which the wave lengths in meters obtained from Table II are plotted as abscissae with the corresponding values of $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{I_0}$ as ordinates, shows the effect of concentration on the dispersion effect. For the value $\overline{\Lambda}_{I\omega}/\overline{\Lambda}_{I_0} = 0.5$ the wave lengths 1.16 m, 11.6 m, and 116 m correspond to the concentrations $\gamma = 0.01$, $\gamma = 0.001$ and $\gamma = 0.0001$ respectively. For these wave lengths the dispersion effect has reduced the electrical force of relaxation to half its value in the stationary case. The effect of concentration on the dispersion effect is most simply expressed by saying that the times of relaxation are inversely proportional to the concentrations.

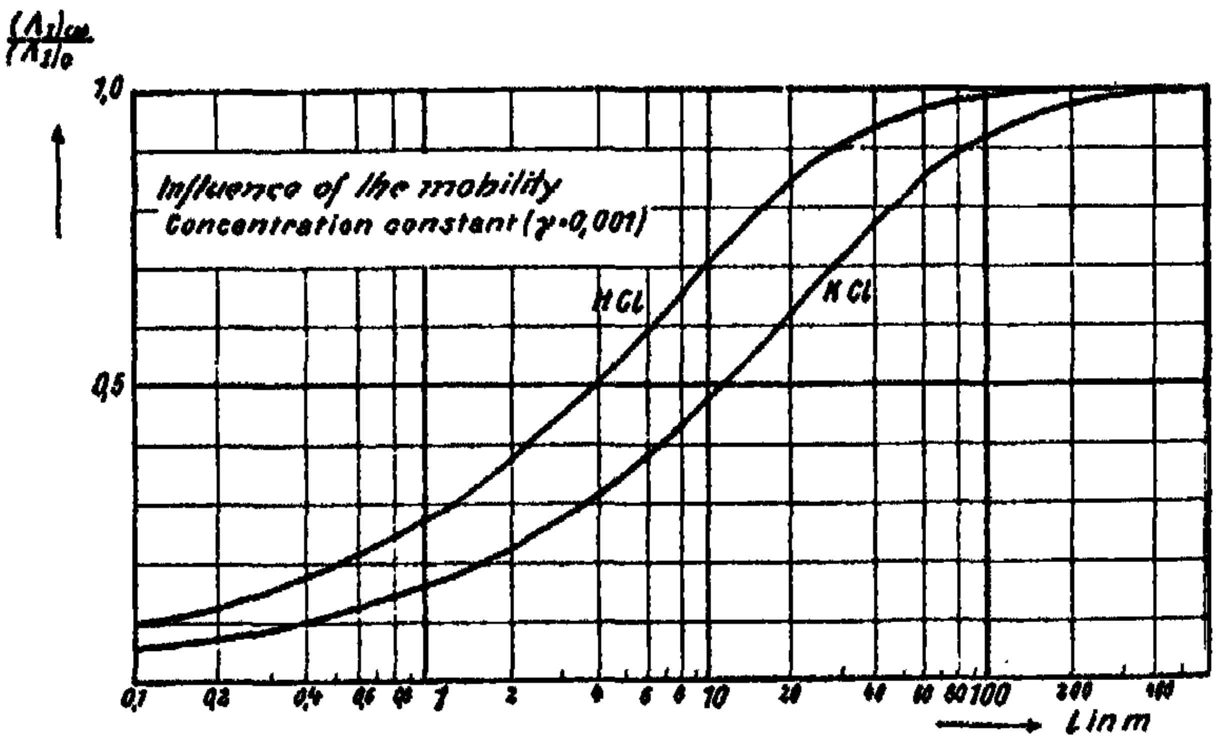

FIG. 4

Influence of the Mobility

The influence of different mobilities on the dispersion effect can be described by means of 0.001 molar solutions of HCl and KCl in water at 18°C. From the tables the corresponding molecular conductances at infinite dilution are

$$\overline{\Lambda}_{\infty HCl} = 380; \qquad \overline{\Lambda}_{\infty KCl} = 130$$

By means of Table IV the times of relation are

$$\Theta_{HCl} = 0.189 \times 10^{-7} \text{ sec.}; \qquad \Theta_{KCl} = 0.553 \times 10^{-7} \text{ sec.}$$

The value of q is again 0.5. From the interpolation Table II and according to Table IV, the values of $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ are given as functions of the wave length. The result of the calculation is given in Fig. 4. It is at once evident that for the same wave length the values of $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ for HCl are much smaller than for KCl.

Influence of the Dielectric Constant

In this case 0.001 molar solutions of KCl in the solvents water and methyl alcohol at 25°C will be considered. The dielectric constants are, respectively,

$$D_{H_2O} = 78.8; \; D_{MeOH} = 30$$

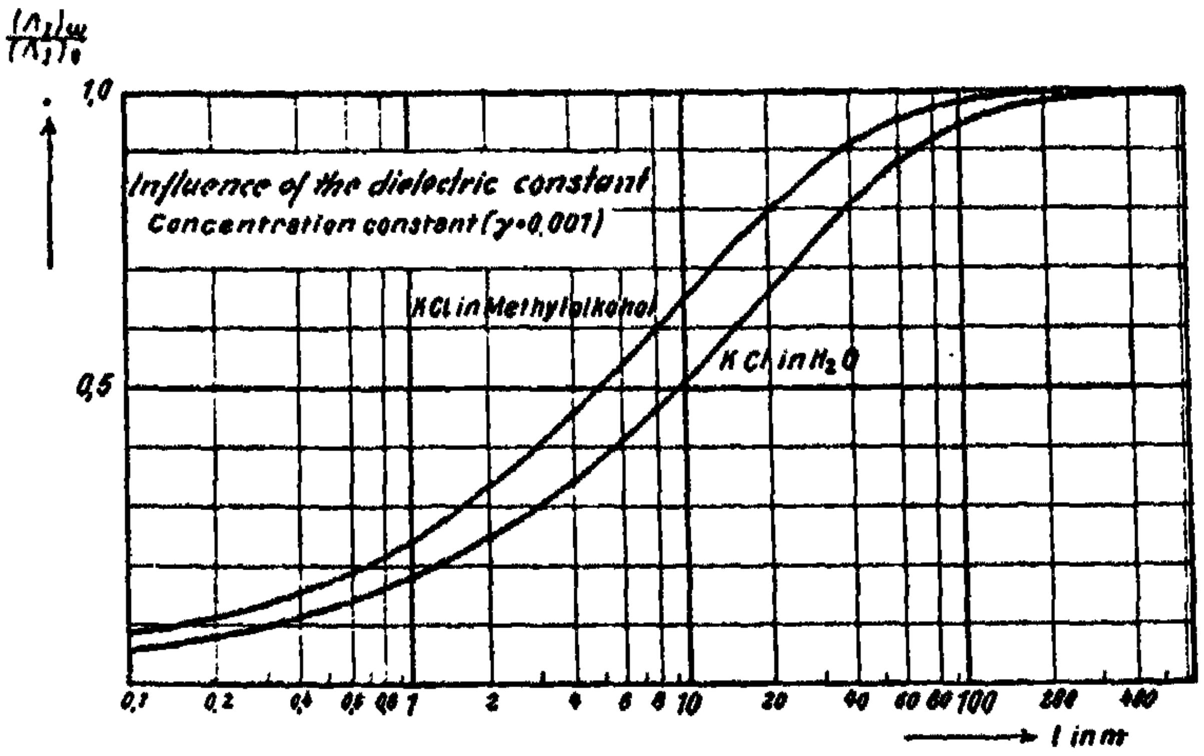

Fig. 5

The molecular conductances at infinite dilution are

$$\bar{\Lambda}_{\infty H_2O} = 150; \; \bar{\Lambda}_{\infty (MeOH)} = 108$$

The latter value was taken from the research of Fraser and Hartley.[12] The times of relaxation are

$$\Theta_{H_2O} = 0.466 \times 10^{-7} \text{ sec.}$$
$$\Theta_{MeOH} = 0.245 \times 10^{-7} \text{ sec.}$$

Again q = 0.5. By means of the interpolation table $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ as a function of the wave length is obtained. The result is shown in Fig. 5. In the case of the methyl alcohol there corresponds to the same $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ value a smaller wave length.

Influence of Temperature

To illustrate the effect of temperature data for water solutions for LiCl at 18°C and 100°C will be utilized. For the mobilities of the ions the following values are used

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[12] Fraser and Hartley: Proc. Roy. Soc., 109A, 351 (1925).

Li^+ at 18° = 33
Li^+ at 100° = 117
Cl^- at 18° = 65
Cl^- at 100° = 208

Equation 6 gives for the κ^2 values

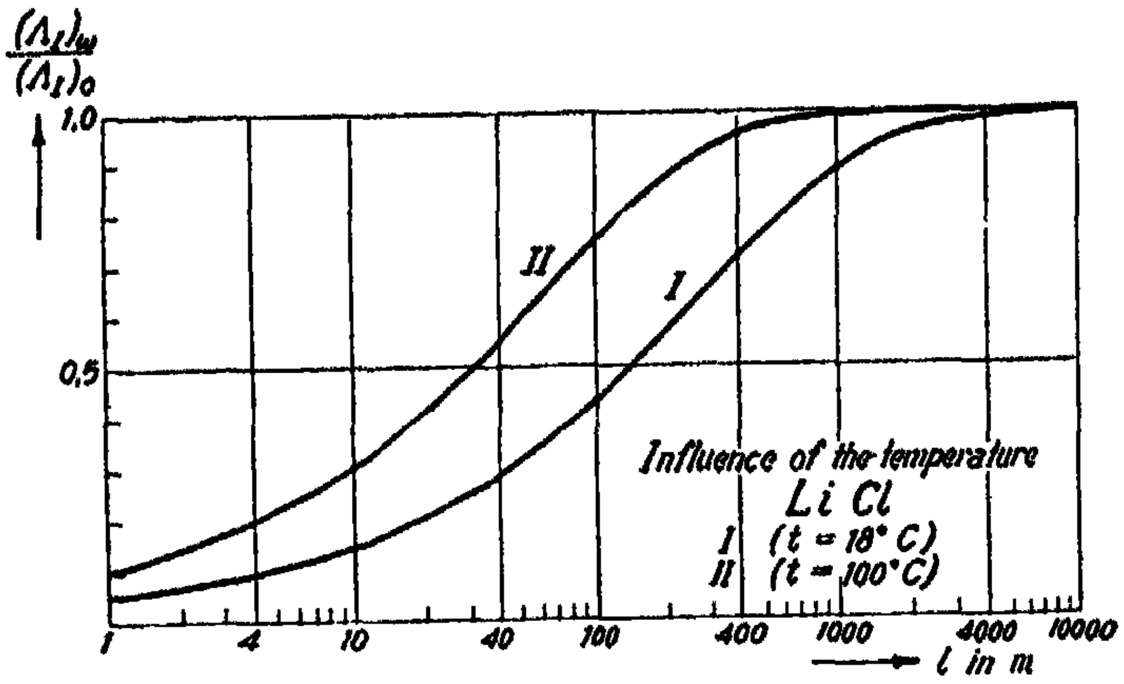

Fig. 6

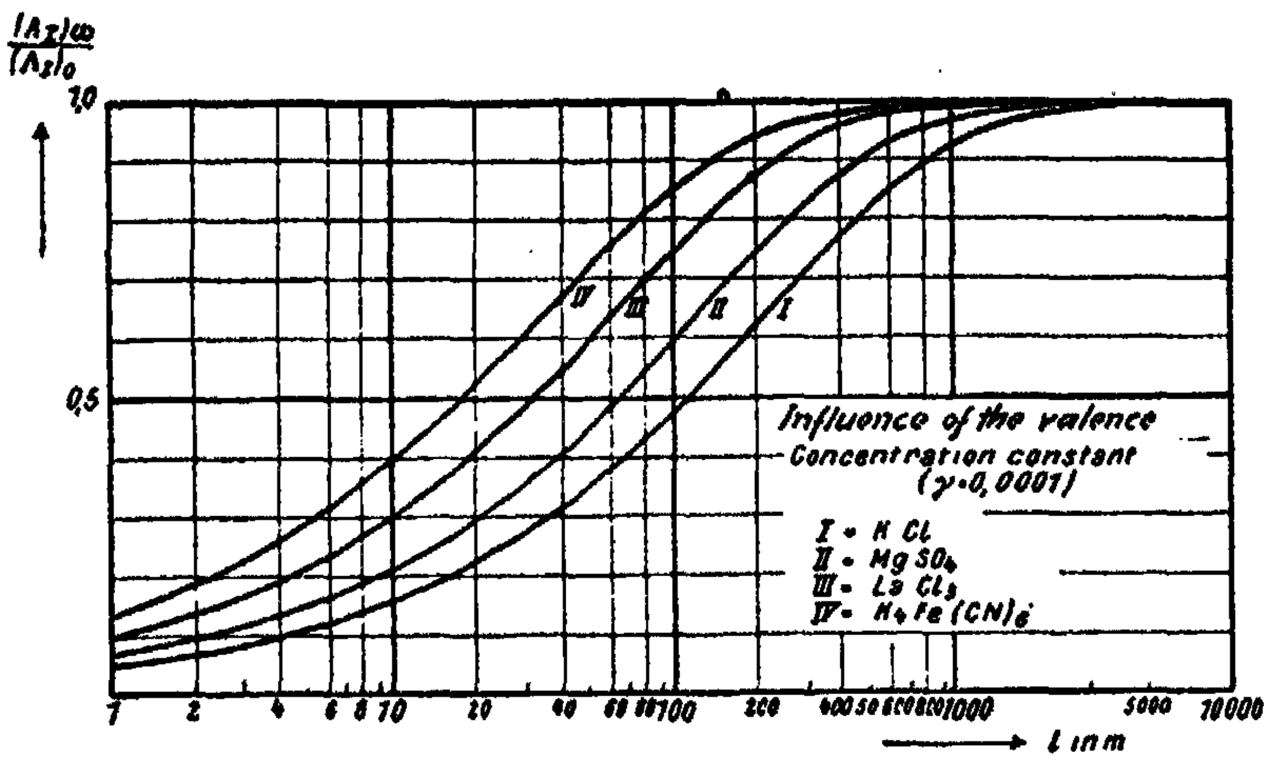

Fig. 7

$$\kappa^2_{(18)} = 0.1068 \times 10^{16}\,\gamma;\ \kappa^2_{(100)} = 0.1170 \times 10^{16}\gamma$$

The corresponding times of relaxation are

$$\Theta_{(18^\circ)} = \frac{0.734 \times 10^{-10}}{\gamma}\ ;\ \Theta_{(100^\circ)} = \frac{0.158 \times 10^{-10}}{\gamma}$$

As in the previous cases $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ can now be expressed as a function of the wave length. The result for $\gamma = 0.0001$ is given in Fig. 6. At the higher temperatures appreciably smaller wave lengths go with the same $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ values.

Influence of Valence

To this point symmetrical electrolytes have been considered. Considering the case of unsymmetrical electrolytes, it will be seen that the valence also affects the dispersion of conductance. In this section are considered electrolytes of the valence types 1-2, 2-2, 1-3, 1-4, and 2-4 for the concentration $\gamma = 0.0001$. For unsymmetrical electrolytes $q \neq 0.5$. According to Table IV the times of relaxation for the various types differ greatly from one another. The differences in q values, and especially the differences in times of relaxation govern the influence of the valence. In Fig. 7, are given the results of the calculations. In order not to unnecessarily complicate the figure values for KCl, $CdSO_4$, $LaCl_3$, and $K_4Fe(CN)_6$ only have been shown. The dispersion curve for $MgCl_2$ falls almost exactly along that for $MgSO_4$, very slightly to the left. The dispersion curve for $Ca_2Fe(CN)_6$ would lie between the curves for $K_4Fe(CN)_6$ and $LaCl_3$. The following Table V gives the values of $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ for different wave lengths for the different electrolytes which have been considered.

TABLE V*

Values of $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0}$ for Different Wave Lengths

Wave Length in Meters	KCl	$MgSO_4$	$MgCl_2$	$LaCl_3$	$Ca_2Fe(CN)_6$	$K_4Fe(CN)_6$
1	0.055	0.070	0.070	0.08	0.116	0.138
2	.073	.098	.102	.12	.167	.190
5	.115	.154	.162	.19	.260	.295
10	.163	.216	.225	.28	.353	.40
20	.230	.30	.309	.39	.478	.53
50	.355	.455	.465	.58	.676	.73
100	.48	.60	.610	.72	.815	.86
200	.63	.75	.758	.85	.925	.95
500	.82	.91	.915	.96	.983	.986
1000	.925	.970	.970	.98	.997	.997
2000	.978	.994	.994	1.	1.	1.
5000	1.	1.	1.	1.	1.	1.
10000	1.	1.	1.	1.	1.	1.

* The values given in Table V are accurate to within 2%.

The values of $\bar{\Lambda}_{I_0}$ are known from equation 4a. In Table VI have been collected values for $\bar{\Lambda}_{I_0}$ and $\bar{\Lambda}_{II}$ for the different types of electrolytes studied. From this table the quantities $\bar{\Lambda}_{I_0}$ and $\bar{\Lambda}_{II}$ for each concentration may be obtained at once.

TABLE VI

Values of $\bar{\Lambda}_{I_0}$ and $\bar{\Lambda}_{II}$ (Different Valence Types)

Valence Type	$\bar{\Lambda}_{II}$	$\bar{\Lambda}_{I_0}$	t°C
1–1	$50.5\ \sqrt{\gamma}$	$0.224\ \bar{\Lambda}_\infty\sqrt{\gamma}$	18
1–2	262.4 "	0.677 " "	18
2–2	404.0 "	1.79 " "	18
1–3	743.0 "	1.52 " "	18
1–4	1890.0 "	2.12 " "	25
2–4	2485.0 "	6.32 " "	25

If the molecular conductances at infinite dilution $\bar{\Lambda}_\infty$ for the strong *electrolytes considered in this section are introduced into the above table,* Table VII results. There have been included in this table values of the quantity $\bar{\Lambda}_{I_0}$.

TABLE VII

Values of $\bar{\Lambda}_{II}$ and $\bar{\Lambda}_{I_0}$ (Different Electrolytes)

Electrolyte	$\bar{\Lambda}_\infty$	$\bar{\Lambda}_{II}$	$\bar{\Lambda}_{I_0}$	t°C
KCl	130	$50.5\sqrt{\gamma}$	$29.1\sqrt{\gamma}$	18
HCl	380	50.5 "	85.2 "	18
LiCl	98	50.5 "	22.0 "	18
$MgCl_2$	222	262.4 "	150. "	18
$MgSO_4$	229	404.0 "	410. "	18
$LaCl_3$	345	743.0 "	524. "	18
$K_4Fe(CN)_6$	680	1890.0 "	1440. "	25
$Ca_2Fe(CN)_6$	620	2485.0 "	3920. "	25

Finally it is of interest to make certain remarks concerning the magnitude of the dependence of the electrical conductance on the wave length or frequency used. The magnitude is recognized most simply when the difference between the molecular conductance for the frequency ω and that for the frequency zero is compared to the molecular conductance at infinite dilution. In Fig. 8 are included data for solutions of $CdSO_4$ at 18°C and $K_4Fe(CN)_6$ at 25°C, γ being 0.0001 in each case. For the $CdSO_4$ solution the molecular conductance is 228.6 according to Table III. The $\bar{\Lambda}_{II}$ value is 4.04 (1.8% of $\bar{\Lambda}_\infty$) and $\bar{\Lambda}_{I_0}$ is 4.09 (1.8% of $\bar{\Lambda}_\infty$). The total lowering of the conductance ($\bar{\Lambda}_\infty$) is, therefore, 3.6%. An increase in the molecular conductance at this concentration of about 0.9% should be observed using the wave length l = approximately 60 m for which $\bar{\Lambda}_{I\omega}/\bar{\Lambda}_{I_0} = 0.5$

The example of $K_4Fe(CN)_6$ is similar. The molecular conductance at infinite dilution (25°C) is

$$\bar{\Lambda}_\infty = 680$$

Further

$$\bar{\Lambda}_{I_0} = 13.7 \ (2.0\% \text{ of } \bar{\Lambda}_\infty)$$

$$\bar{\Lambda}_{II} = 18.9 \ (2.8\% \text{ of } \bar{\Lambda}_\infty)$$

The total lowering of the molecular conductance is 4.8%. An increase of about 1% in the molecular conductance should be observed using the wave length l = approximately 16.3 m, for which $\bar{\Lambda}_{I\omega}/\Lambda_{I_0} = 0.5$. The maximum dispersion effect (extremely short wave lengths) to be observed would be of the order of magnitude of 2%.

At higher concentrations, using suitable wave lengths, a greater increase in the molecular conductance should result. However, since the theory in its present form is applicable only to very dilute solutions, it is evident that one cannot resort to measurements upon these more concentrated solutions to verify the theory. The authors believe that when the terms of higher order have been considered the concentration region which may be treated will be increased, though one may not say how much at this writing. It may be recalled that the activity theory has been treated in this manner by several investigators with the result—apparently at least—that the concentration range to which it may be applied has been considerably broadened.

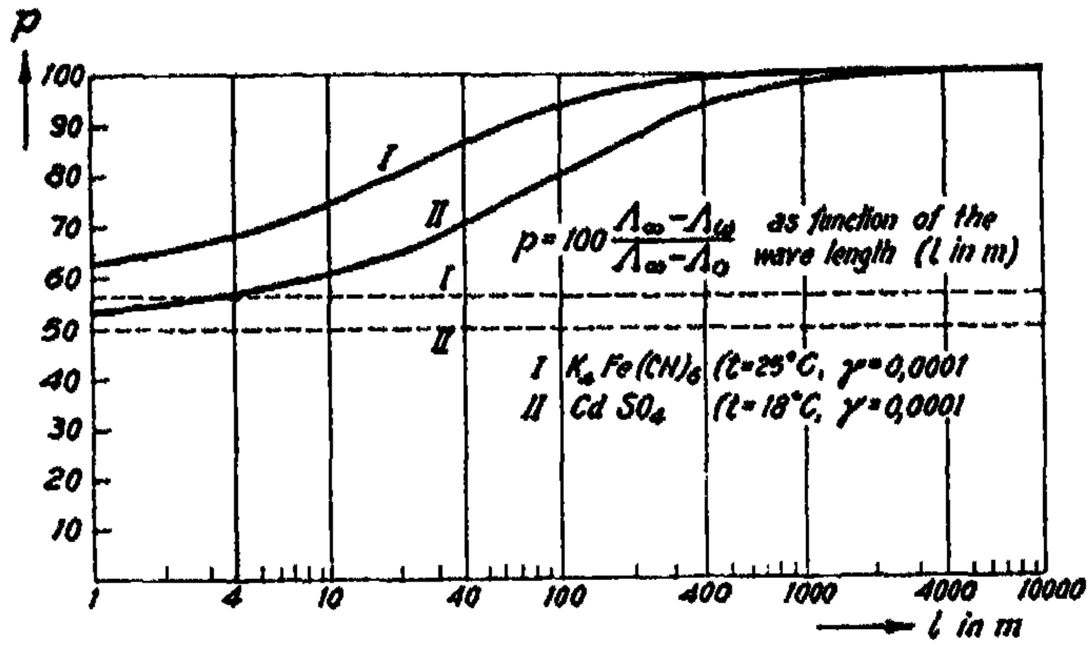

FIG. 8

The authors wish to thank Professor P. Debye of this Institute for the interest shown and counsel given by him during the course of the work.

Leipzig, Germany,
Madison, Wisconsin.

PHOTOCHEMICAL OXIDATION WITH POTASSIUM DICHROMATE[*]

BY D. S. MORTON

The reaction between quinine and potassium dichromate in a solution containing sulphuric acid has been studied as a photochemical oxidation by Luther and Forbes,[1] who reached the conclusion that only the light absorbed by the quinine was active, the chromic acid functioning merely as an inner light filter. "We chose the reaction between quinine and chromic acid, already studied by Goldberg,[2] whose results seemed to show that the velocity was dependent on the quantity of light absorbed by the chromic acid. Experiments with monochromatic light soon convinced us that quinine was the substance sensitive to light, and that the chromic acid acted only as an indifferent light filter, absorbing a part of the light and turning it into heat. . . .

"Since the yellow ray is very slightly absorbed by the reaction mixture, it cannot cause appreciable chemical change; hence experiment (1) indicates that the dark correction is adequate, and the consistency of the following results points to the same conclusion. The blue ray is virtually inactive; in the table, correction is made for 0.02 [406] which filter B transmits. The violet and the ultraviolet rays are active, and the constancy of the results in the last column show that the photochemical action is proportional to the incident light in each case. . . .

"The figures thus far exhibited prove (1) that the amount of chemical change in each unit of time is proportional to the fraction of a given ray absorbed by quinine in the same period. (2) the amount of light absorbed by the chromic acid has no effect on the result. From (1) and (2) the apparent inertness of the blue ray is no longer surprising. (3) No sensible error is involved in finding the light reaction by difference. . . .

"From these figures it is inferred that the photochemical reaction takes place in two stages: first, the formation of sensitized quinine with a velocity proportional only to light absorption; then a reaction in the ordinary sense between this product and chromic acid and of sulphuric acid, as in the dark reaction. At very small concentrations[3] the second stage is so slow that it determines the speed of the reaction as a whole; but when $C_2 > 0.0013$ the speed of the second stage is very great and the speed with which sensitized quinine is produced regulates the progress of the reaction; this sensitizing

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[*] This paper is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established at Cornell University by August Heckscher.

[1] J. Am. Chem. Soc., **31**, 770 (1909).

[2] Leipzig dissertation (1906).

[3] [C_2 is the concentration of chromic acid in gram equivalents per liter ($Cr_2O_3/3$ = 33.4 grams)].

is probably a reversible reaction, otherwise the product would accumulate rapidly when C_2 became small and prevent any approach to a reaction of the first order. Finally, the smaller the value of C_2, the more in proportion should the hydrogen ion accelerate the photochemical reaction as a whole. . . .

"The percentages of each ray passing through the light filters, and the percentages absorbed by quinine and by chromic acid, respectively, in each experiment, are calculated. The speed of the light reaction is proportional to the quantity of light of given wave-length absorbed by the quinine alone unless the concentration of chromic acid is very small; this is consistent with the hypothesis that the light reaction runs in two stages."

There is no hedging about these conclusions and there is also no recognition of the fact that the results call for explanation. The general accuracy of Luther and Forbes' experiment is, of course, beyond question; but their conclusions cannot be the whole truth, because there are technical processes[1] based on the photosensitivity of potassium dichromate.

"When mixed with organic substances, potassium dichromate is reduced on exposure to light; gelatine under such circumstances is rendered insoluble. This reaction is taken advantage of in the 'carbon' process of photography. The gelatine is mixed with a pigment of any colour and the paper carrying this film is sensitised by floating on a solution of potassium dichromate. On exposure under a negative, the gelatine becomes insoluble in those portions exposed to the light, and retains the pigment, while the portions protected by the darker portions of the negative are almost unacted upon, and may be dissolved in warm water. In this manner photographs of great beauty and permanence may be produced. . . . The insoluble gelatine does not absorb water, but will take oil, which may be mixed with any desired pigment and thus becomes the basis of the oil and bromoil processes. Gum, mixed with dichromate, is also made insoluble by exposure to light, and this is made use of in photography in the gum dichromate process."

The conclusions of Luther and Forbes have been questioned by Plotnikow,[2] though perhaps not with the definiteness that one would like. He showed that light, which was absorbed by an ammonium bichromate solution, causes this solution to oxidize alcohol. He also offered a tentative explanation for the failure of Luther and Forbes to obtain normal results.

"It is to be assumed that both components will be photochemically active when quinine is oxidized by chromic anhydride in acid solutions; the reaction also takes place in the dark. Many of the active rays, such as the violet and the ultra-violet, for instance, are absorbed by both components, in consequence of which the chemically active light of these wave-lengths is divided between the two components. It is not impossible that the two bands of photochemical absorption, which belong to the quinine and the chromium are masked to some extent by thermal absorption. [It is questionable whether this means anything at all.] From what has been said it is evident how com-

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[1] Thorpe: "Dictionary of Applied Chemistry," **2**, 241 *(1921)*.

[2] "Lehrbuch der Photochemie," 198, 215 (1920).

plicated this reaction must be. Since the light absorption is middling strong, it will hardly be possible to formulate for this reaction a differential equation which can be integrated. It is therefore not surprising that the investigators [Luther and Forbes] who have studied this reaction without considering all the factors have not obtained any agreement between experiment and theory."

Apparently as an after-thought, Plotnikow says, four short paragraphs later, that "it would be rather interesting to study the oxidation of quinine by chromates, $K_2Cr_2O_7$ or K_2CrO_4, in neutral solutions. One would probably get simpler relations and the pure photochemical properties of the two components would be recognized more easily."

Unfortunately Plotnikow never tested this suggestion of his and it evidently seemed of no importance to Luther and Forbes, because, in a later paper, Forbes, Woodhouse and Dean[1] discuss Plotnikow's mathematical relations, which are of no special importance, and ignore entirely the fundamental question why the chromic acid should apparently be photochemically insensitive.

Both constituents in the reaction must be photochemically active, as Plotnikow points out. If one of them is not, it must be because the experimental conditions are so abnormal that the photosensitiveness of one constituent apparently disappears. As a matter of fact, the conditions under which Luther and Forbes worked were most extraordinary. All their reacting solutions were 5.4 N in sulphuric acid, while the dichromate concentration was always less than 0.01 N. It has long been known that the oxidizing power of a dichromate solution increases with increasing acidity. Only recently it was shown by Vincent,[2] in experiments on the electrolysis of potassium dichromate solutions that this salt does not act as a depolarizer in neutral solution with platinum electrodes, there being one hundred percent evolution of hydrogen at the cathode. The depolarizing action appears and increases as sulphuric acid is added, and is nearly complete for a saturated solution of potassium dichromate in normal sulphuric acid. It seemed probable that, by using 5.4 N sulphuric acid, Luther and Forbes had pushed the oxidizing power of the dichromate to the limit, so that the absorption of light could produce no appreciable additional activation.

In order to test this assumption experiments were made with potassium dichromate and ethyl alcohol. If the concentrations are chosen rightly, this makes a very satisfactory photochemical experiment. An ordinary hand-regulated D.C. carbon arc spotlight A, operated at 50 amperes served as the source of light, Fig. 1. The rays were made to converge, by means of glass lenses L_1, L_2 and mirror M on the bottom of the glass absorption cell C. (6 × 6 × 6 cm), which contained the reacting mixture. The outer cell F (6 × 10 × 10 cm), supported in the position shown, contained the liquid employed as light-filter. The contents of F were kept cool by circulating

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[1] J. Am. Chem. Soc., 45, 1891 (1923).

[2] J. Phys. Chem., 29, 875 (1925).

cold water through a spiral copper tube T immersed in the liquid. Cell C was provided with a glass cover D, silvered on the top surface. For the dark reaction a similar combination of cells was used. They were protected from light and were maintained at approximately the same temperature as the cells in which the light-reaction was studied.

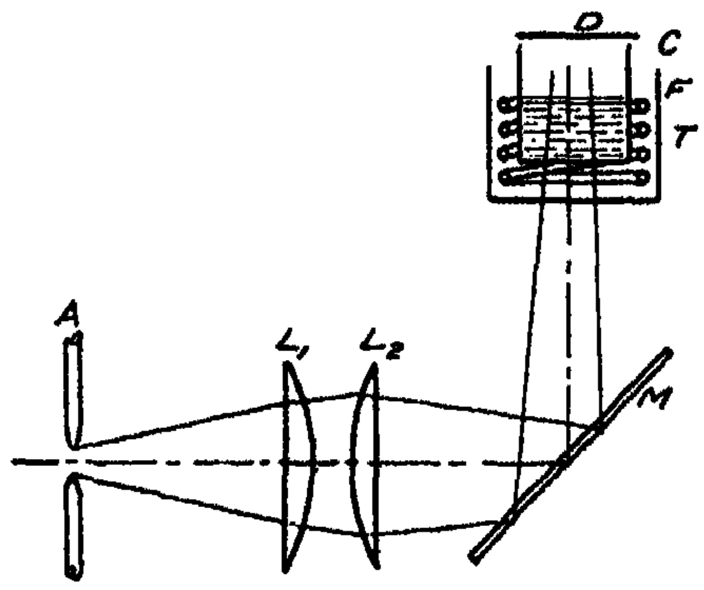

Fig. 1

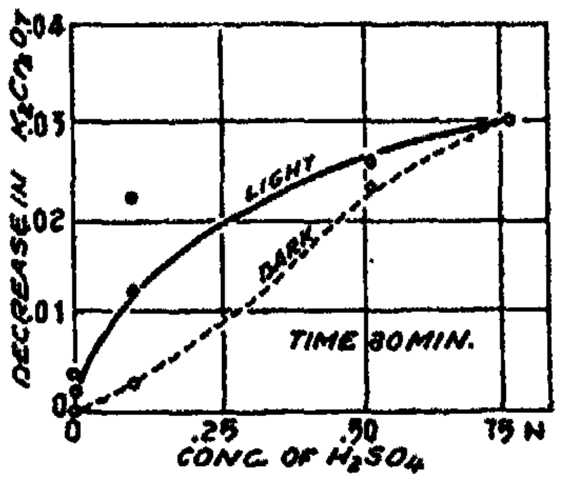

Fig. 2
Curve 1. 5% alcohol, 0.04 N $K_2Cr_2O_7$

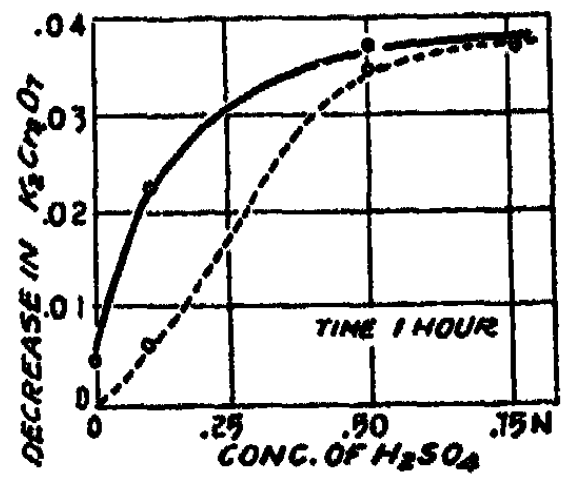

Fig. 3
Curve 2. 5% alcohol, 0.04 N $K_2Cr_2O_7$

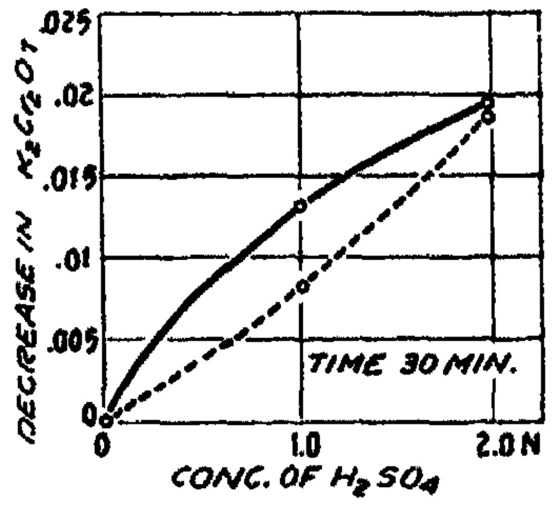

Fig. 4
Curve 3. 1% alcohol, 0.025 N $K_2Cr_2O_7$

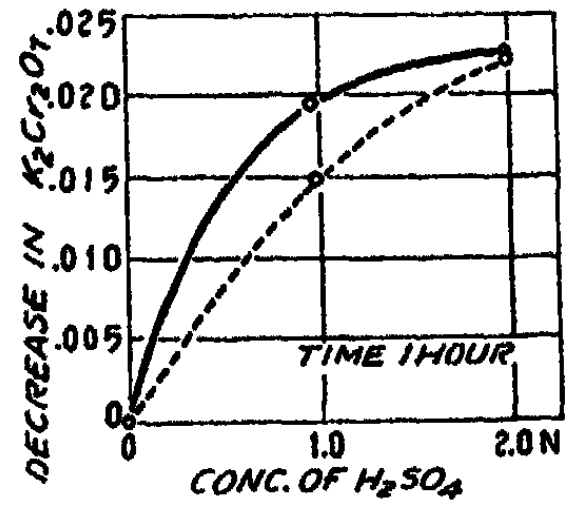

Fig. 5
Curve 4. 1% alcohol, 0.025 N $K_2Cr_2O_7$

Kahlbaum's pure potassium dichromate was used and 95% ethyl alcohol. Neither was purified further. The volume of the reacting solution was 100 cc. in all cases. The course of the reaction was followed by withdrawing samples at intervals (usually every fifteen minutes) and determining the concentration of dichromate iodimetrically. Experiments with water and with alcohol as light-filters showed no appreciable difference, so any activation of the alcohol by light of the visible spectrum is negligible. A potassium bichromate filter brings the light-reaction to a stand-still, thus showing that the dichromate is the photosensitive substance. The photochemical reaction is not prevented by a copper sulphate filter, showing that the light which is absorbed by the dichromate is the photochemically active light.

The observed amounts of reaction in the light and in the dark, with varying initial concentrations of sulphuric acid are given in Table I and II, and shown graphically in Figs. 2-5 in which the decrease in concentration of dichromate is plotted as ordinates against concentration of sulphuric acid as abscissas.

TABLE I

5% ethyl alcohol; 0.04 N $K_2Cr_2O_7$

Time minutes	Decrease in conc. of $K_2Cr_2O_7$ in equivalents per liter			
	Neutral		0.1 N H_2SO_4	
	Dark	Light	Dark	Light
30		0.0022	0.0032	0.0128
45				
60	0.0004	0.0044	0.0060	0.0223

Time minutes	Decrease in conc. of $K_2Cr_2O_7$ in equivalents per liter			
	0.5 N H_2SO_4		0.75 N H_2SO_4	
	Dark	Light	Dark	Light
			0.0240	0.0252
30	0.0256	0.0272	0.0322	0.0324
45			0.0370	0.0376
60	0.0352	0.0388	0.0384	0.0388

TABLE II

1% ethyl alcohol; 0.025 N $K_2Cr_2O_7$

Time minutes	Decrease in Conc. of $K_2Cr_2O_7$ in equivalents per liter			
	1 N H_2SO_4		2 N H_2SO_4	
	Dark	Light	Dark	Light
30	0.0085	0.0127	0.0180	0.0189
45				
60	0.0250	0.0196	0.0222	0.0223

With neutral 0.04 N $K_2Cr_2O_7$ and 5% alcohol, the light reaction is approximately ten times that of the dark-reaction at the end of an hour. With 0.1 N H_2SO_4 the light-reaction is more than twice as fast as the other one and the total change in the light is five times as much as in the corresponding neutral solution. With 0.75 N H_2SO_4 the light-reaction and the dark-reaction are practically identical, which means that, under these conditions, the dichromate appears to be photochemically inactive, which is what Luther and Forbes found. With more dilute alcohol and more dilute bichromate, there is a distinct difference between the light-reaction and the dark-reaction with normal sulphuric acid; but this difference is negligible with double-normal sulphuric acid.

The results of Luther and Forbes are absolutely accurate; but they are misleading as stated. When studying the rate of inversion of a dilute cane sugar solution by acids, we are justified in saying that, under these conditions, we may treat the concentration of water as practically constant; but it would be inaccurate to say that water does not enter into the reaction. Luther and Forbes were quite justified in saying that, under their conditions, chromic acid could be treated as practically insensitive photochemically; but it was unfortunate to imply, as they do, that chromic acid is photochemically insensitive in the reaction between quinine and chromic acid. The general relation seems to have escaped them entirely, even after it had been suggested to them by Plotnikow.

It has seemed desirable to straighten out this matter because even Kistiakowsky[1], who should be the last word in photochemistry, has failed to recognize the limitations in the work of Luther and Forbes and accepts it as right without any reference to sulphuric acid changing the general relations.

"An interesting, but not completely explained, photochemical reaction is the oxidation of quinine by chromic acid in presence of sulphuric acid. This reaction was studied by Goldberg,[2] who noticed a very small temperature coefficient (1.02). It was later the object of an extensive investigation by Luther and Forbes,[3] which revealed interesting relations.

"Not only quinine, but also chromic acid, absorbs the light which is causing the photochemical reaction. . . . Luther and Forbes measured the absorption coefficient (a) of both substances and demonstrated, by applying equation 1, that the light absorbed by chromic acid is ineffective; the latter is therefore acting only as an inner screen. The authors demonstrated, further, that the rate of reaction was proportional to the amount of light energy absorbed by quinine and was independent of the chromic acid concentration, at least when this latter was varied from 0.012 to 0.001N. At still lower concentrations of chromic acid, a decrease in the rate of reaction was observed. . . .

"Recently Forbes and his co-workers[4] have extended the earlier experiments of Luther and Forbes and studied in particular the influence of sulphuric acid. They found that the rate of reaction is practically independent

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[1] "Photochemical Processes," 39 (1928).

[2] Z. wiss. Phot., 4, 56 (1906).

[3] J. Am. Chem. Soc., 31, 770 (1909).

[4] J. Am. Chem. Soc., 45, 1891 (1923).

of the concentration of sulphuric acid, only, however, if this is above 0.5 normal; in more dilute solutions, a decrease in the rate of oxidation approximately proportional to the concentration of the acid was observed."

The reason why Kistiakowsky did not detect the weak point in the experiments of Luther and Forbes is apparently because he is not interested at all in the conditions for a photochemical reaction to take place, but only in the kinetics of a reaction which does take place. Practically all he says on this point is that "only in the nineteenth century was the first and fundamental law of photochemistry deduced. Grotthuss published in 1817 a paper which contained a clear outline of this law. As formulated by him, the law states that only light which is absorbed can produce chemical change. Grotthuss' paper attracted little attention on the part of his contemporaries, and in 1839 Draper derived independently the same law and supported it by experiments on the hydrogen-chlorine reaction."

There is not a word said about the experiments of Grotthuss on depolarizers or about the later formulation that all light which is absorbed by a substance tends to eliminate that substance and that what actually happens is a question of chemistry. Instead Kistiakowsky jumps to the question of light quanta.

"A starting point for the rapid development of photochemistry along new lines was undoubtedly the introduction of quantum theory. General attention turned from rather unsuccessful thermodynamic speculations to a quantitative study of photochemical kinetics, resulting in a deeper understanding of the rôle of radiant energy in producing chemical changes and in many valuable contributions to the general theory of chemical kinetics."

Without questioning any of this, the fact remains that Kistiakowsky's view-point is defective to the extent that the contradiction between the results of Luther and Forbes and the behavior of bichromated gelatine either never occurred to him or did not seem to him of any importance.

The general results of this paper are:

1. Under suitable conditions dichromate solutions are photochemically active for light which is absorbed by the dichromate.

2. With increasing acidity the oxidizing power of the dichromate solution increases and the apparent action of the light consequently decreases.

3. With ethyl alcohol, potassium dichromate, and varying amounts of sulphuric acid, the light-reaction can be made practically the whole thing or practically zero as one wishes.

4. Since Luther and Forbes studied the photochemical oxidation of quinine by chromic acid in 5.4N sulphuric acid, they were working under conditions which should and did make the chromic acid practically photochemically insensitive.

5. The conclusions of Luther and Forbes in regard to the photochemical activity of chromic acid are right for the extreme conditions under which they worked; but they are not generally true and are consequently misleading.

Cornell University.

THE SURFACE PROPERTIES OF SOAP SOLUTIONS*

BY WALTER C. PRESTON AND A. S. RICHARDSON**

The foaming tendency of aqueous solutions of soap and various other substances has long been the subject of scientific study. Most workers in this field have agreed in focusing attention upon the peculiarities of the surface film of the solution and many important facts have been discovered regarding its composition, structure and physical properties.

It was early foreseen that the formation of stable bubbles from soap solutions must be associated with a concentration of soap at the surface exposed to air. Leidenfrost, in 1756, attempted to explain the peculiar properties of the soap bubble by postulating a preferential concentration of the fatty material in the surface of the soap solution,[1] thus strangely foreshadowing the idea—so attractive to students of soap solutions—of a surface layer of oriented molecules which, a century and a half later, was developed by Hardy, by Langmuir, and by Harkins. In a general way, it may be accepted that solutes which impart foaming properties tend to concentrate in the surface layer of the solution and hence in the foam itself, but this fact, considered alone, is of no great value in distinguishing solutions which foam readily from those which do not, as will appear below.

As shown both by thermodynamic reasoning and by actual experiment, the concentration of a solute in the surface layer is accompanied by a decrease in surface tension. The fact that soap lowers the surface tension of water has frequently been invoked to explain, at least partially, the foaming tendency of soap solutions. Since, however, there are aqueous solutions, such as acetic acid solution, which do not foam readily in spite of having low surface tension comparable with that of soap solutions which foam copiously, it is evident that neither low surface tension nor the concentration of solute in the surface is, of itself, a sufficient explanation of foaming.

Recognizing the inadequacy of low surface tension to explain foaming tendency, some investigators have assumed and attempted to demonstrate the importance of high viscosity, especially surface viscosity, as a basic property underlying high foam power.

The idea of a tough surface skin, a superficial viscosity as distinguished from that of the interior, is even an older concept, though less widely known, than the concept of surface tension, which was proposed by J. A. von Segner[2]

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** Chemical Division, The Procter and Gamble Company, Ivorydale, Ohio.

[1] Leidenfrost: "De aquae communis nonnullis qualitatibus tractabus," Duisburg, 1756. See article on Capillary Action in Encyclopedia Britannica.

[2] von Segner: Comment. Soc. Reg. Göttingen 1, 301 (1751). See article on Capillary Action in Encyclopedia Britannica.

in 1751. The basic idea of surface viscosity is generally attributed to Descartes[1] and, in its more precise form, has been developed by Plateau[2] and a number of other investigators.

In general, different investigators have been inclined to assign to these two properties, low surface tension and high surface viscosity, the chief role in accounting for the lathering of soap solutions. Some interesting modifications of this view have been urged, but these will best be considered after the experimental part of the present paper.

Originally it was the hope of the writers that, following a simultaneous study of surface tension, surface viscosity, and foam power, there might appear among these properties some more precise relationship than has heretofore been observed. As a matter of fact, prolonged investigation failed to develop any such relationship and the majority of the experimental results, being thus of a negative character, are scarcely worth presenting in detail. However, it may be worth while to record a few fragments of the work which go farther than mere failure to establish a positive correlation and suggest that foam power cannot ever be explained in terms merely of surface tension and surface viscosity.

Experimental

Measurements of Surface Viscosity

An oscillating disk, suspended by a torsion wire, was used for measuring surface viscosity. Its construction followed so closely the description given by Stables and A. E. Wilson[3] and by R. E. Wilson and Ries[4] that detailed description in the present paper is unnecessary. A simplified sketch of the apparatus is given in Fig. 1. In operation, the monel metal disk was lowered into the surface of the liquid by means of a micrometer screw capable of controlling the depth of immersion to within 0.01 mm. and, starting with an initial torque of 215°, the amplitude of successive oscillations was observed with the aid of a pointer, rigid with the disk, moving in a horizontal plane over a fixed circular scale. The moment of inertia of the oscillating system, determined by the method of removable disks of known weight as described by Wilson and Ries, was 1444 ± 3. The temperature of the water bath was constant at 30°C ± 0.1°. The authors are indebted to Dr. C. H. Milligan for valuable aid in the construction of this instrument especially, also for aid in the preparation and planning of some of the other apparatus used in this study.

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[1] Descartes: "Les Mémoires." 1638.

[2] Plateau: "Statique des Liquides"; Pogg. Ann., **141**, 44 (1870); Luvini: Phil. Mag., (4), **40**, 190 (1870); Meyer: Pogg. Ann., **113**, 55, 193, 383 (1861); Oberbeck: Wied. Ann., **11**, 634 (1880); Marangoni: Pogg. Ann. **143**, 342 (1871); Stables and Wilson: Phil. Mag., (5), **15**, 406 (1883); Quincke: Wied. Ann., **35**, 592 (1889); Shutt, Ann. Physik, (4), **13**, 714 (1904); Metcalf: Z. physik. Chem., **52**, 1 (1905); Rohde: Ann. Physik, (4) **19**, 935 (1906); Shorter: Phil. Mag., (6) **11**, 317 (1906); **17**, 560 (1909).

[3] Loc. cit.

[4] Wilson and Ries: First American Colloid Symposium, 245 (1923).

The viscosity of a solution, as measured by the rotating disk method, is expressed by the formula of Stables and Wilson, $v = Kd/t$, where v = relative viscosity (with no absolute significance whatsoever), K = moment of inertia of the oscillating system, t = period of oscillation, and d = logarithmic decrement, i.e., the logarithm of the ratio of the amplitude of one oscillation to the amplitude of the next succeeding oscillation.[1]

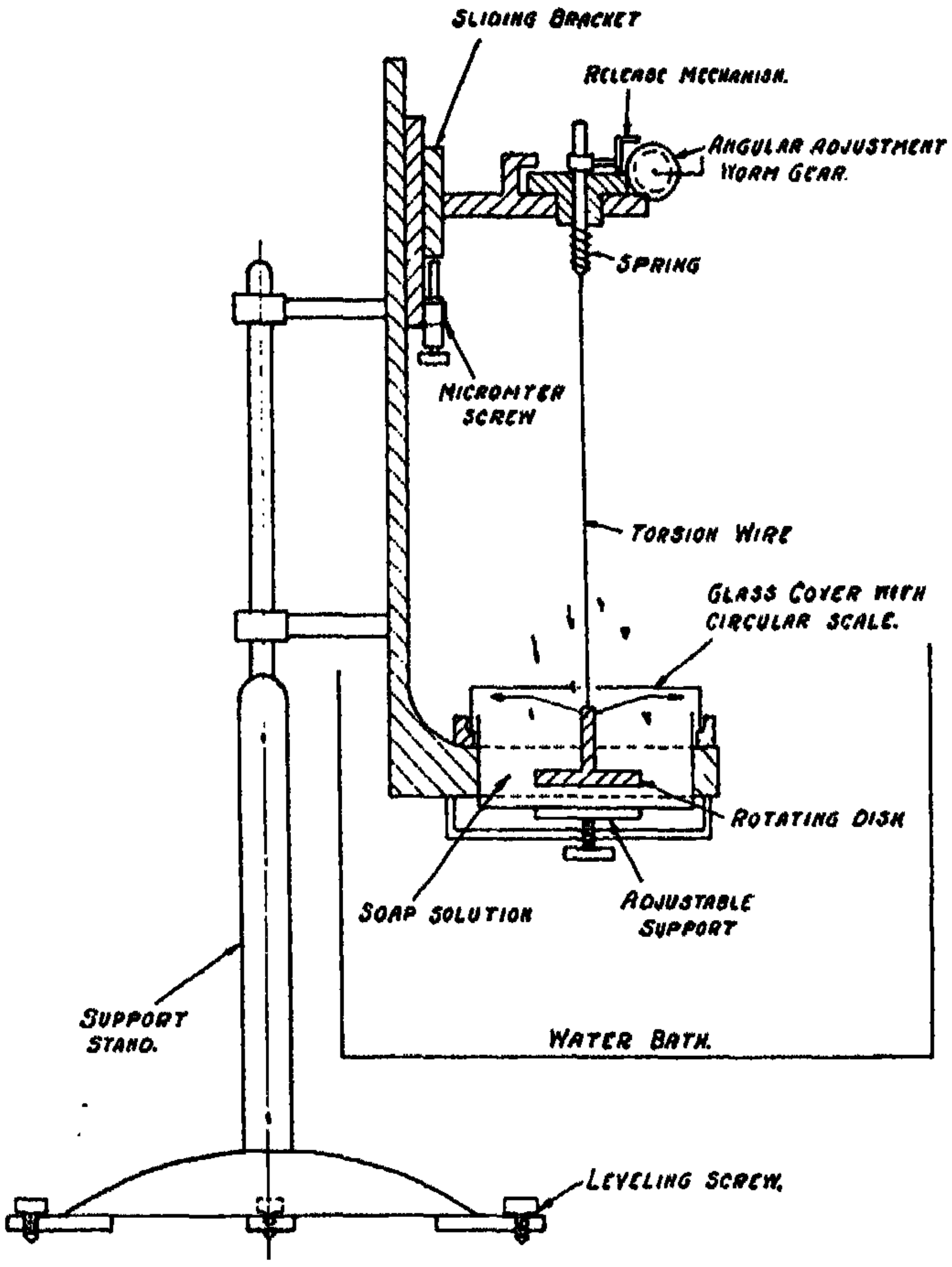

FIG. 1
Surface Viscosimeter

Measurement of Surface Tension

There is considerable controversy over the proper choice of method for determining surface tension. Since the formation of foam is a dynamic

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[1] For convenience, the position of the pointer was noted only at the end of each swing in one given direction and the magnitude of the oscillation was calculated by doubling the difference between this reading and the position of rest. The separate measurement of each oscillation in opposite directions is of doubtful theoretical advantage and puts an undesirable extra load upon the operator. After all, results by this method are relative, not absolute.

process, a dynamic method of measuring surface tension was preferred in the present work and the drop method was chosen. Two dropping tips were used, with radii 0.3175 (±0.0010) and 0.290 (±0.0015) cm., respectively. The bottom surfaces were ground and the sides were highly polished. Under 40 diameter magnification, the larger tip showed no imperfections, but the smaller showed several slight flaws around the edge, although perfect to the naked eye. The rate of formation of drops, ordinarily 20 in 15 to 20 minutes, was controlled by opposing a suction to gravity. Temperature was controlled within a range of 1°C. Surface tension values were calculated with the aid of Harkins' correction curve.[1] The Harkins correction factor, $r/V^{\frac{1}{3}}$, lay between 0.71 and 0.73 for distilled water, and between 0.96 and 1.1 for most of the 0.1% soap solutions used.

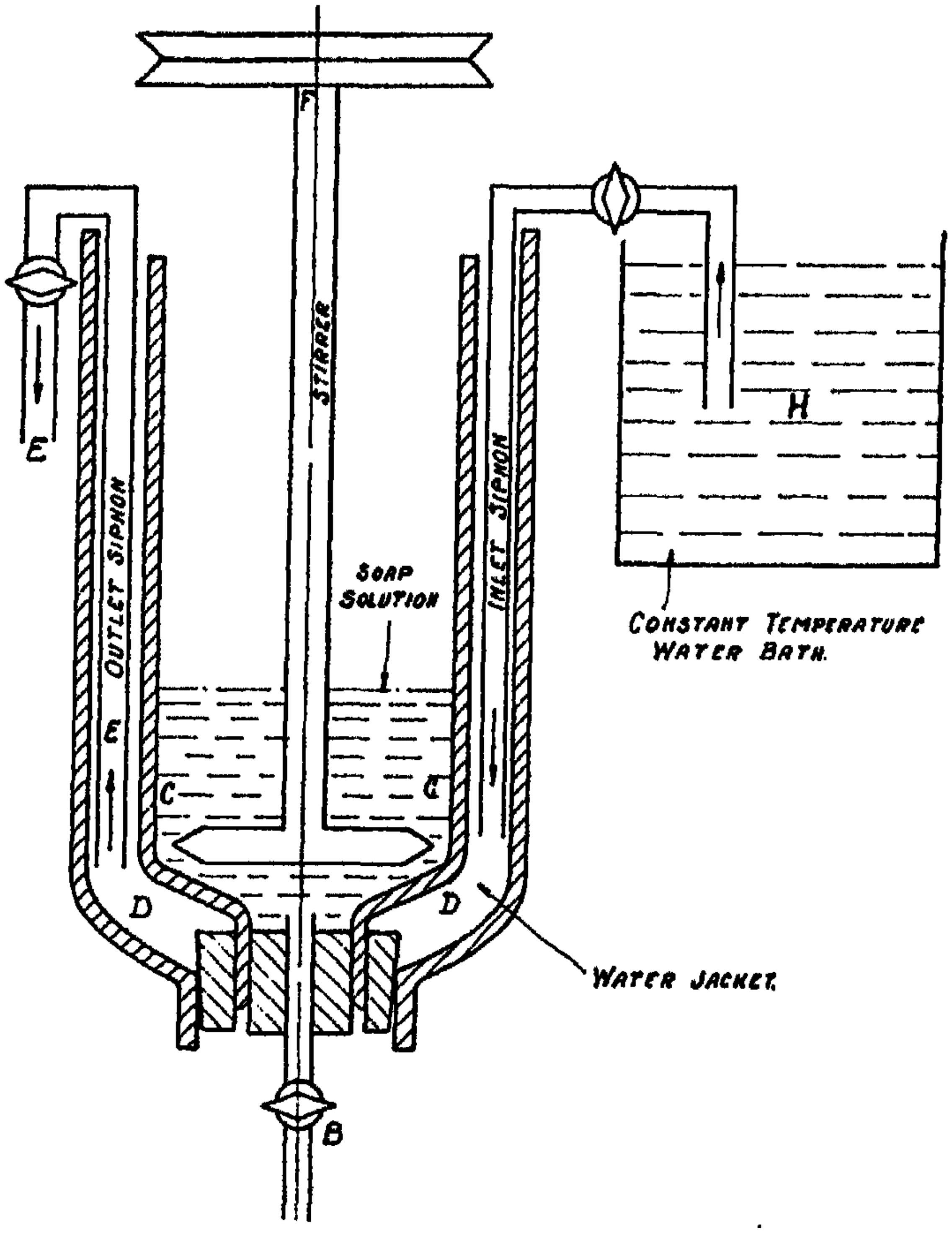

FIG. 2
Apparatus for measuring Foam Power

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[1] Harkins: J. Am. Chem. Soc., 41, 417 (1919).

Measurement of Foam Power

For the measurement of foam power, use was made, after some modification, of apparatus previously assembled and used by Mr. W. E. Price for the same purpose. The apparatus is shown in Fig. 2. The temperature of the water jacket "D" is held at 30°C ± 1° by siphoning in warm water from "H," and siphoning out the excess thru "E." In operation, 100 c.c. of soap solution is poured into the bell jar "C," and agitated for 2 minutes, at a speed of 2000 R.P.M. by the stirrer "F," consisting of a shaft of 1/4" brass pipe, to the bottom of which is welded the horizontal piece of brass tubing with ends flattened to narrow openings. Air is drawn down the hollow shaft and thrown out from the horizontal blades by centrifugal force. After two minutes, stirring is stopped, and at one minute intervals the clear liquid which drains from the foam is drawn off thru the stopcock "B" into a graduated cylinder. The volume of liquid so collected, subtracted from the original volume (100 c.c.) gives the percent of the solution converted into and remaining in the foam. This value has been found more quantitatively measurable and reproducible than measurements of the volume of foam produced by stirring or shaking. The "foam power" recorded in the table below is the per cent of the solution retained as foam after standing one minute.

Comparison of the Three Types of Soap

Table I records surface viscosity, surface tension, and foam power measurements of soaps representing three important commercial types, as follows:

No. 1. A typical white toilet soap, the fatty acid characteristics being: Saponification value 217; iodine value 52.5; titre 32.0°C.

No. 2. A typical yellow laundry soap, the fatty acid characteristics being: Saponification value 189.3; titre 35.0°C; rosin content about 1/3 of total acids; iodine value of fatty acids, exclusive of rosin, 53.3.

No. 3. A typical olive oil soap of textile grade, the fatty acid characteristics being: Saponification value 193; iodine value 79; titre 21.3°C.

These soaps were not used in their commercial forms, but the liberated free fatty acids were resaponified with the theoretical amount of pure NaOH and made into a 3% stock solution of the soap. From these stock solutions,

TABLE I

Surface Viscosity, Surface Tension, and Foam Power of 0.1% Soap Solution at 30°C

	No. 1 White Toilet Soap		No. 2 Yellow Laundry Soap		No. 3 Olive Textile Soap		Distilled Water
	Fresh	Exposed	Fresh	Exposed	Fresh	Exposed	
Foam Power, %	84	26	82	10	71	17	0
Surface Viscosity	24.6	24.5	23.6	6.7	6.6	6.8	6.8
Surface Tension dynes/cm.	24.7	24.8	23.7	23.7	23.3	23.4	70.5
Hours exposed to air	0	48-51	0	24-30	0	23-24	0-48

the dilute solutions for testing were prepared by a uniform procedure of diluting, boiling, uniform cooling, and storing for one hour in glass-stoppered bottles at 3°C before use.

Aging the 0.1% soap solutions in closed vessels produced unimportant differences in the experimental results. However, aging the solutions in open vessels, protected from appreciable quantities of dust but exposed to the gradual diffusion of air, produced very significant variations. While attention in the present paper is directed to the change in physical properties of the solutions, is may be of interest to note in passing that the underlying chemical change is apparently due to the absorption of carbon dioxide from the air.

Surface Tension and Foam Power:

The three soap solutions described in Table I show practically the same surface tension, while soaps #1 and #2 when fresh show appreciably greater foam power than soap #3, a set of facts which alone is sufficient to cast doubt upon any precise correlation between surface tension and foam power. The lack of any such simple correlation is more conclusively shown by comparison of the fresh solutions with those exposed to the air. The aged soap solutions show, within experimental error, the same surface tension as the fresh solutions, while the foam power of all the aged solutions is distinctly low.

Surface Viscosity and Foam Power:

The somewhat superior foam power of the fresh solutions of soaps #1 and #2 as compared with soap #3 seems, at first glance, to be associated with the greater surface viscosity of soaps #1 and #2. However, soap #3, having only the surface viscosity of water itself, is not greatly inferior in foaming properties to the other soaps showing almost four times the surface viscosity of water. This alone is sufficient to show that the relationship between surface viscosity (as measured by the oscillating disk method) and foaming tendency is not a simple one. This lack of a simple relationship is again conclusively demonstrated by a comparison of the fresh and aged solutions. Upon exposure to air, the solution of soap #1 gradually loses its foam power with no appreciable change in surface viscosity, while soap #2 also loses its foam power but, unlike soap #1, loses also its high surface viscosity. The fresh solution of soap #3 is a very much better foamer than the aged solution of soap #1 in spite of the fact that the surface tensions of the two solutions are approximately equal and the surface viscosities actually in the opposite order of their foam power.

In general, the relationship between foam power and measurable specific properties of soap solutions is very much more obscure than has been heretofore recognized. Certainly the combined concepts of surface tension and surface viscosity are inadequate to explain foaming tendency.

The results given above are easily reproducible and are typical of a large number of experiments. Many variations were tried without substantial effect upon the final conclusions. These variations included the substitution of the commercial soaps for the pure soaps, variations in the exact method of preparing the soap solutions, in the time of formation of the drops, in the surface tension measurements, and in the depth of immersion of the oscillating disk, stirring the surface surrounding the disk, etc.

The surface layer causing the high surface viscosity must form very rapidly, as stirring produced little effect upon the viscosity value. Slight variations from the standard depth of immersion (0.5 mm.) would not have been vital, as shown by Table II.

TABLE II

Effect of Depth of Immersion of Oscillating Disk. 0.1% Solution, Soap No. 1, at 30°C

Depth of Bottom of Disk	Surface Viscosity
0.0 mm.	26.9
0.5 "	27.0
1.0 "	27.6
2.0 "	28.6
2.5 "	29.6
Disk submerged entirely	12.4

Some surface tension measurements were made in which the time of drop formation was varied. In case one soap is adsorbed more rapidly in the surface than is another, the more rapid adsorption might be associated with better foaming properties. Lord Rayleigh[1] many years ago concluded that no appreciable adsorption of sodium oleate occurs within the first 1/100th second after the formation of the surface, as determined by his vibrating jet method.

While the drop weight method becomes unreliable when the drops are rapidly formed, yet if a difference existed between two soaps, one of which foamed well and the other poorly, it should be possible to demonstrate this difference at least qualitatively by this method. In Fig. 3 are given results with distilled water and with 0.1% solutions of soap #1 which had been (a) protected from the air, thus retaining high foam power, and (b) exposed to the air, with consequent loss of high foam power. It will be seen that the rate of change of surface tension with drop-time is the same with both solutions. Thus the rate of surface adsorption, as indicated by surface tension measurements with drop-times of from 0.5 to 60 seconds, does not distinguish between the fresh and the aged solutions, good foamers and poor respectively.

Surface Plasticity and Foam Power:

Among the interesting modifications of the conventional ideas of surface viscosity is that of R. E. Wilson and Ries,[2] who suggest that the stability of foam is dependent upon the resemblance of the surface layer to a plastic solid rather than a viscous liquid. They have cited the increase in logarithmic decrement of the oscillating disk with decreasing amplitude as evidence of the plastic solid condition of the surface. Fig. 4 shows typical runs, the logarithm of the amplitude of oscillation of the disk being plotted against the number

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[1] Rayleigh: Proc. Roy. Soc., 47, 281 (1890).

[2] Loc. cit.

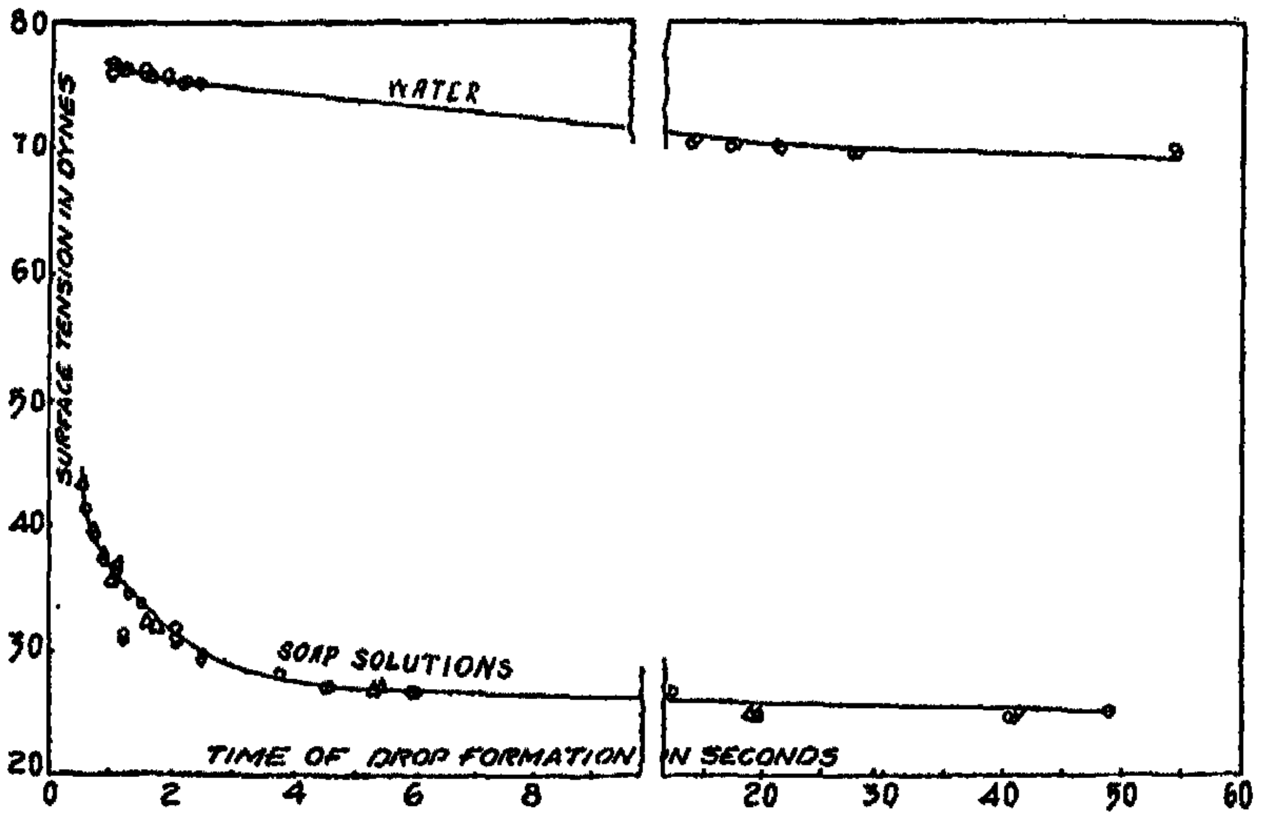

Fig. 3
Showing change in surface tension with change in time of drop formation
0.1% Solutions of Soap No. 1 at 30°C.
⊙ Fresh, unexposed solutions.
△ Solutions exposed to air 24 hours.

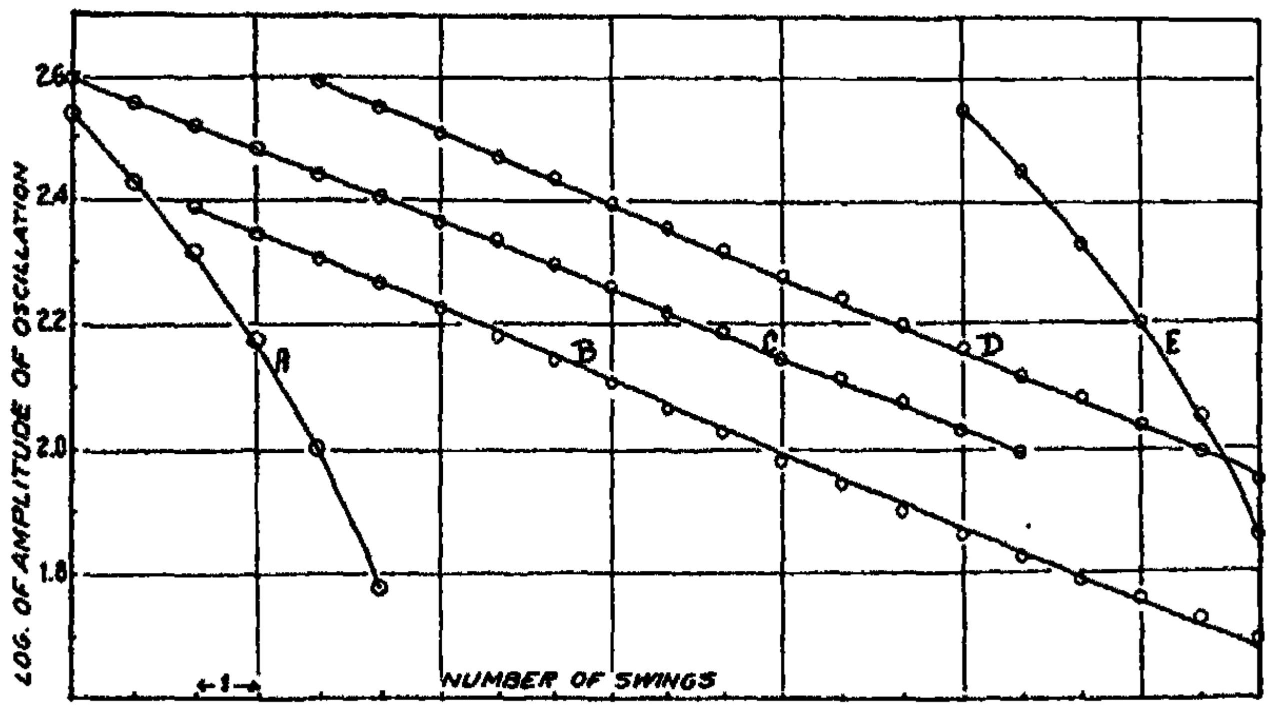

Fig. 4
Curves showing rate of damping of oscillating disk

Curve	A—Soap No. 1—Both fresh and aged.	Surface viscosity	24.5
"	B—Distilled Water	" "	6.9
"	C—Soap No. 3—Both fresh and aged	" "	6.8
"	D—Soap No. 2—Aged	" "	6.8
"	E—Soap No. 2—Fresh	" "	23.5

of swings. Only in the case of water, soap #3 (the sodium oleate type), and the exposed solution of soap #2 is the logarithmic decrement constant, as indicated by the straightness of the line; in solutions possessing high surface viscosity, the curves are concave toward the X-axis. However, this curvature is not affected by the aging of the solution of soap #1, even to the point of almost destroying its foam power. Theoretically, the increase in logarithmic decrement in such experiments as those of Wilson and Ries and those in the present paper is good evidence of the plastic solid condition of the surface layer. However, if this condition be regarded as a cause of stable bubble formation and high foam power, it predicts zero foam power for soap #3 and predicts that fresh and aged solutions of soap #1 should have the same foam power, conditions quite contrary to the facts observed.

The concepts of surface tension and surface viscosity as conventionally understood fail to explain the tendency of solutions to foam. If useful correlations between the physical properties of the surface of solutions and their tendency to foam are to be established, fresh ideas are needed—radically new concepts, perhaps, or at least distinctively new applications of established concepts.

Marangoni,[1] Rayleigh,[2] Milner,[3] Shorter[4] and others have urged that capability of local variations in surface tension by variations in thickness, concentration, etc. of the surface film is essential to the stability of a foam. This is a stimulating line of thought; but, up to the present, it is little more than the germ of an idea.

Summary

Simultaneous measurement of surface viscosity, surface tension, and foaming power have been made on soap solutions of several distinctive types, before and after prolonged exposure to air. The results obtained show that there is no simple correlation among these properties. While all soap solutions show low surface tension, this property alone does not necessarily involve tendency to foam. Even the combination of low surface tension and high surface viscosity or plasticity does not necessarily confer high foaming power upon a solution. On the other hand, solutions of high foaming power sometimes show no greater surface viscosity than that of water itself. Unknown factors besides surface tension and surface viscosity determine the foaming power of soap solutions.

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[1] Loc. cit.

[2] Rayleigh: Phil. Mag., **48**, 331 (1899).

[3] Milner: Phil. Mag., **13**, 96 (1908).

[4] Shorter: Phil. Mag., **27**, 718 (1914).

THE SORPTION OF WATER VAPOUR BY ACTIVATED CHARCOALS
PART II. ISOTHERMALS IN PRESENCE OF AIR

BY A. J. ALLMAND, R. CHAPLIN AND D. O. SHIELS

1. Introductory

In most of the published work dealing with sorption isotherms of vapours on solid sorbents, foreign gases have been excluded, some kind of a vacuum technique being used. Patrick and Opdycke,[1] however, employed a dynamic or streaming method when studying the sorption of certain vapours by silica gel and, in particular, the same method was used by Berl and Andress[2] with water vapour and a Bayer soft wood charcoal (activated by zinc chloride). Apart from this last paper, the only published work of which we are aware dealing with the system water vapour—charcoal in presence of air is due to Rakovsky[3] and to Katz[4], both of whom allowed previously dehydrated charcoal to stand in a desiccator over sulphuric acid solutions of various concentrations, and followed the change in weight until the latter had become constant. Rakovsky used a number of different specimens of charcoal (blood charcoal, untreated and previously extracted in various ways; bone charcoal; sugar charcoal; lime-wood charcoal; coconut charcoal), whilst Katz employed Merck's animal charcoal. All these authors worked at room temperature, and carried out both absorption and desorption experiments, i.e. after the specimen of charcoal had been allowed to come into equilibrium with saturated aqueous vapour, it was dehydrated in stages by replacing the water

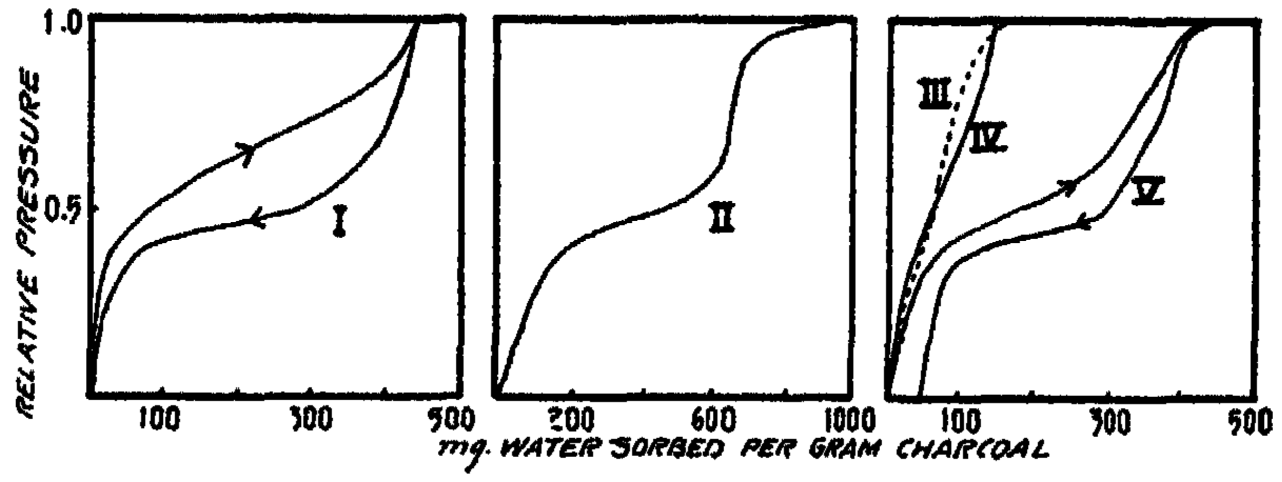

Fig. 1

I Berl and Andress. Sorption and desorption curves.
II Katz. Mean of sorption and desorption curves.
III Rakovsky. Coconut charcoal. Sorption curve.
IV Rakovsky. Sugar charcoal. Sorption curve.
V Rakovsky. Blood charcoal. Sorption and desorption curves.

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[1] J. Phys. Chem., 29, 336 (1925).

[2] Z. angew. Chem., 34, 369 (1921).

[3] J. Russ. Phys. Chem. Soc., 49, 371 (1917).

[4] Proc. Amsterdam Acad., 26, 548 (1923).

in the air-stream saturators or in the desiccator by sulphuric acid of continually increasing concentration until the water vapour pressure was again reduced practically to zero.

Fig. 1 contains the results of Berl and Andress and of Katz, together with some of the curves obtained by Rakovsky.

Relative pressures (P/p_0—the ratio of the water vapour pressure used to that of saturated aqueous vapour at the temperature of the experiment—have been plotted against milligrams of water taken up per gram of charcoal. In every case, isotherms were obtained with an inflexion at intermediate pressures which is characteristic of water-vapour, and in every case pronounced hysteresis was found, i.e. the adsorption and desorption curves were not coincident, the latter being further from the pressure axis than the former. In addition, many of the curves obtained, but not all, showed a second inflexion at higher relative pressure than the first. It may be added that Rakovsky did not limit himself to carrying out one sorption-desorption cycle, but repeated the process on the identical specimen of charcoal. His interesting results in this connection will be referred to later.

2. Behaviour of Charcoals on heating in Air and in Vacuo

The charcoals used by us have been described in detail in Part I[1] of this work, and little need be added. Table I contains the percentage losses in weight of the different charcoals (as taken from stock) found on different occasions

(a) on heating to constant weight in an air-oven at 140°C.
(b) on thorough evacuation at about 270°C.
(c) on thorough evacuation at about 800°C.

TABLE I

	140° C.	270° C.	800° C.
Charcoal A.	15.19; 15.32	15.09; 15.70	18.67; 17.00
From birchwood—air-activated		18.18; 15.99	28.6 ?
Charcoal B.	33.80; 33.50	29.11; 29.72	
From pinewood—$ZnCl_2$ activated		34.07	—
Charcoal C.	20.38; 20.43	21.45	23.70; 23.62
From coconut—steam activated			24.53

With one exception—the high figure obtained for Charcoal A at 800°, possibly due to an air leak in the apparatus—the variations shown by any set of figures fall within the limits corresponding to normal differences in

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[1] J. Phys. Chem., 32, 452 (1928).

humidity in the atmosphere at the times the samples were taken. It will be noticed that the average loss in weight of a charcoal on evacuation at 270° is very similar to the average loss on heating in air at 140°, but that the figures for 800° are appreciably higher. The explanation lies in the tenacity with which the final residues, both of water and adsorbed gases, are held by activated charcoals, as compared with the ease with which the great bulk of the sorbed material is lost.

In the case of Charcoal C, the gases evolved during outgassing at 270° and at 800° were measured and analysed. The following were the results, expressed in cc. of gas per gram of charcoal (measured at room temperature and pressure).

TABLE II

	270°	800°
CO_2	2.25	6.28
O_2	0.95	0.75
CO	0.49	16.73
N_2	6.24	5.99
H_2	—	0.09
Total	9.93	29.84

The absolute quantities of nitrogen are about the same, as was to be expected, it being well known that this gas is not firmly held by charcoal. On the other hand, the volumes of oxides of carbon evolved, particularly of carbon monoxide, are far greater at the higher temperature, in agreement with the results of Rhead and Wheeler.[1] The preponderance of carbon monoxide in the gases given off during the last stages of the high temperature evacuation is shown by the following figures, representing the composition of the last 10 c.c (out of a total of 111 cc.) given off at 800°.

CO_2	1.17 cc.	
O_2	0.00 cc.	
CO	8.52 cc.	
Residue	0.32 cc.	(probably H_2—undetermined owing to an accident to the apparatus)

It may be added that, when raising the temperature of the charcoal during these evacuations, a rush of evolved gas was noticed at about 250°-270° and a second at about 600°C. This is in general agreement with the observations of Lemon.[2]

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[1] J. Chem. Soc., **103**, 461 (1913).

[2] Phys. Rev., (2) **14**, 281 (1919).

3. Rates of Sorption and Desorption

Our experimental method has been described in Part I. Reference will only be made here to the lengths of run found necessary in order to obtain constancy of weight (within the limit of change of 0.1 mg. per gram per hour arbitrarily laid down by us) when passing from one point on an isothermal to another. Possible governing factors were the nature of the charcoal, the temperature at which it had been evacuated prior to experimentation, the values of the aqueous vapour pressures with which the charcoal was in equilibrium at the commencement and end of the particular run and, finally, the nature of the isotherm—whether one of sorption or of desorption. Usually the pressure was altered by steps of 2-3 mm. at a time; under these circumstances, the *total duration of actual passage of moist air over the charcoal sample* found necessary before the weight of the charcoal had readjusted itself to the new conditions varied between 5 and 250 hours. If lengthy periods, during which the charcoal container was shut off and allowed to stand, were alternated with successive periods of passage of moist air, the total length of run, as just defined, tended to decrease. Similar, shorter, periods were, of course, inherent in the method of experimentation, and make any accurate comparison of the sorption and desorption velocities under the different conditions impossible. Measuring, however, the rate of sorption or desorption, not merely in terms of the length of time required for equilibrium to be set up when passing from one point on an isothermal to another, but by *the weight of water taken up or lost per gram of charcoal per hour* (during the passage of the stream of water vapour) *divided by the difference between the water vapour equilibrium pressures* (in mm.) *at the beginning and end of the run*, the following conclusions have been come to.

(a) These rates, in the great majority of cases, were less than 0.5 mg. of water vapour per gram of charcoal per mm. pressure difference per hour—they rarely exceeded 0.7 mg.

(b) Under the conditions of experiment, it can be said in general that sorption is rather less rapid than desorption at low and at medium pressures, and more rapid at higher pressures.

(c) There is little difference shown between charcoals evacuated at 270° and those evacuated at 800°.

(d) There is remarkably little difference between the three charcoals employed.

(e) For any given isothermal, the maximum rate of sorption or desorption is to be found in that intermediate pressure portion over which a small pressure difference corresponds to a large change in amount sorbed (see later). This is a very definite effect.

During any given run, of course, the rate of change of water content decreased in course of time, as a natural consequence of the approach to equilibrium conditions, and finally became very small.[1]

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[1] Cf. Tryhorn and Wyatt: Trans. Faraday Soc., 22, 134 (1926).

4. Example of Experimental Data

The actual equilibrium figures have, naturally, in view of the ill-defined nature of an activated charcoal, no absolute value. The results of one complete experiment only will therefore be tabulated as typical, and the data as a whole expressed by means of isothermal diagrams. Table III contains the figures obtained with Charcoal A (preliminary outgassing at 800°). It must be realised that, as explained in Part I (p. 448), the sorbed weights of water are calculated on the assumption that none of the air originally present in the dry charcoal has been displaced. It is recognised that an error is thereby introduced, but experiments have shown it not to be great, and its exact estimation would have been laborious, and the results of no particular interest.

Table III

Absorption			Desorption		
Aqueous vapour pressure in mm.	Hours required to attain constancy of weight	Mg. of water per gram charcoal	Aqueous vapour pressure in mm.	Hours required to attain constancy of weight	Mg. of water per gram charcoal
5.15	19	11.5	21.60	110	346.9
8.07	21	22.4	19.65	130	326.7
10.60	53	69.9	17.52	104	301.1
13.40	95	158.5	14.90	120	263.5
14.77	100	176.4	13.45	70	245.0
17.15	116	196.5	10.80	70	176.1
19.50	99	250.1	8.33	50	89.7
21.47	100	307.9	5.45	20	51.3
23.76	94	393.3	0.00	18	24.5

5. Results

In what follows are given, for Charcoals A and C, outgassed at (circa) 270° and 800°, and for Charcoal B, outgassed at 270°—

(i) particulars respecting the outgassing process;

(ii) the sorptive power of the charcoal for dry air prior to the passage of the moist air stream;

(iii) the increase in weight of the charcoal, compared with its original evacuated weight, after the final passage of dry air at 25°;

(iv) data concerning the result of subsequent evacuation of the charcoal;

(v) the diagram of the complete sorption-desorption isotherm.

(a) *Charcoal A—evacuated at 270°C.*

(i) This was the first experiment done. The points were not determined in the usual regular order of continually increasing followed by continually decreasing aqueous vapour pressures and, in addition to the initial evacuation, two further ones were carried out during the course of the experiment. No detailed record was kept.

(ii) Three determinations—11.47; 11.13; 12.38 mg./gram.

(iii) 25.1 mg./gram. On another occasion, a specimen of the same charcoal was charged with saturated aqueous vapour at 25°, and then dry air passed over till the weight was constant. The increase in weight in this case was only 15.6 mg./gram.

(iv) Eight hours' evacuation at 250° resulted in recovery of 8.1 mg./gram of water. Further evacuation for 1½ hours between 400°-800°, followed by 1½ hours at 800°, gave another 7.9 mg./gram, making a total of 16.0 mg./gram of water recovered. Non-condensible gases were given off during these evacuations. An accident prevented their recovery.

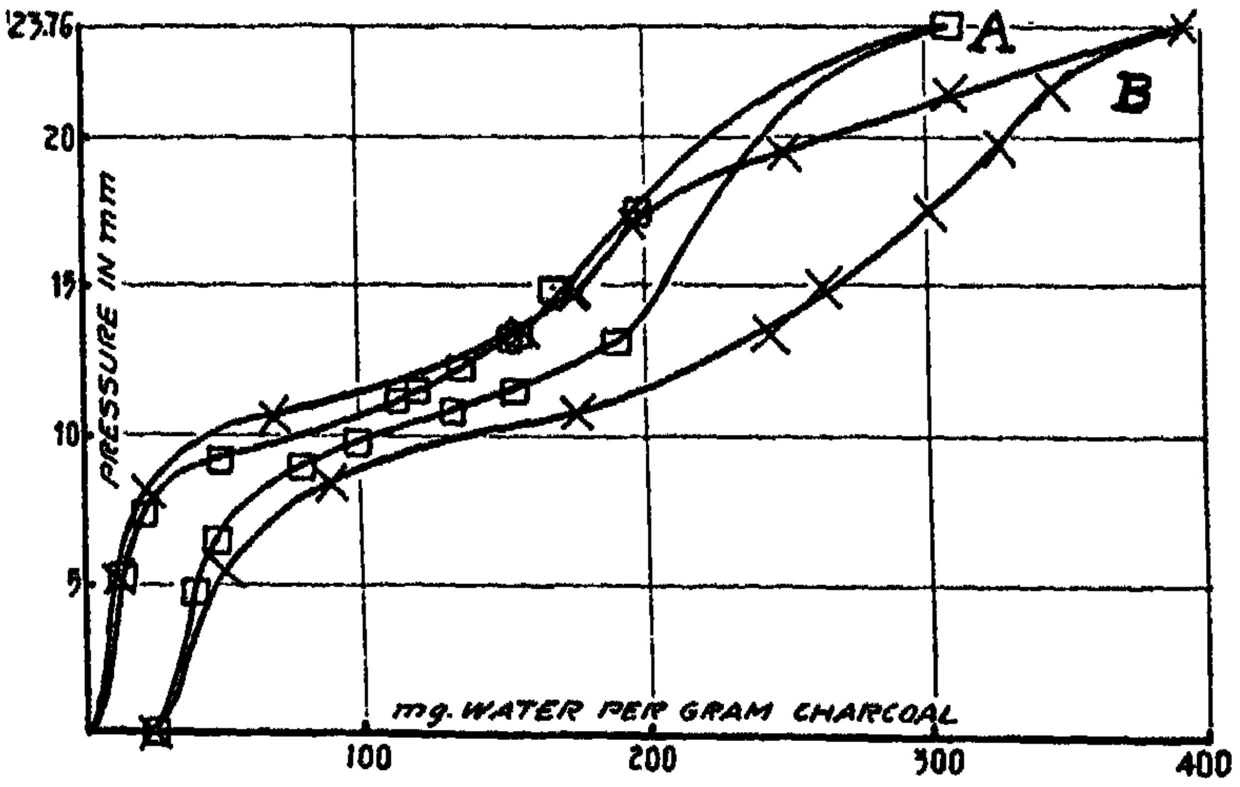

Fig. 2

(v) See Figure 2A. Two experiments were done with a pressure of 17.45 mm. One of these was carried out by direct exposure of a second sample of the same charcoal, after saturation with dry air, to the full water-vapour pressure. The two q values obtained were 198.4 and 202.4 mg./gram. In another run done in duplicate, q was found to be 156.5 mg./gram at 13.40 mm., and 155.0 mg./gram at 13.36 mm. These figures give an idea of the possible degree of reproducibility of results.

(b) *Charcoal A—evacuated at 800°C.*

(i) Outgassed for 3½ hours at 790°-800°.

(ii) 19.42 mg./gram.

(iii) 24.5 mg./gram.

(iv) 0.3 mg./gram only of water recovered by evacuation at 270°. A leak in the apparatus prevented further investigation.

(v) See Fig. 2B.

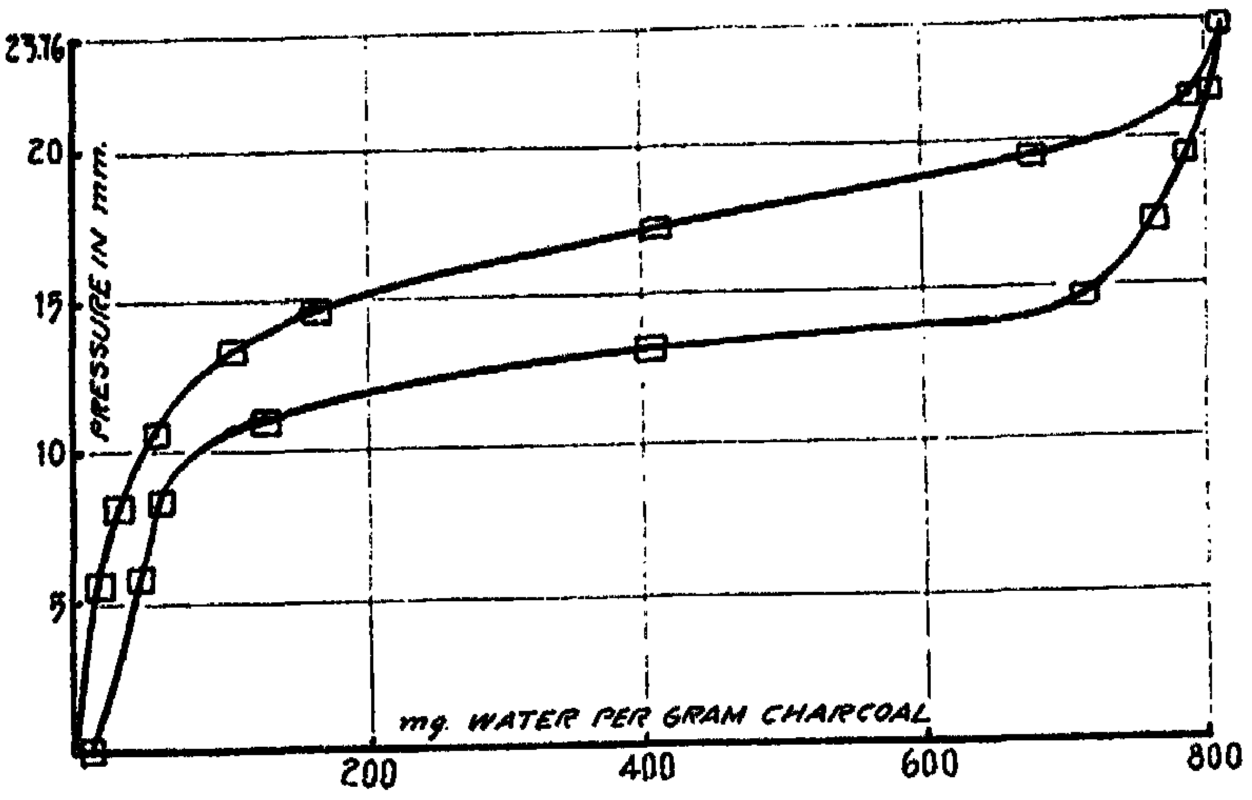
23.76
20
15
10
5
PRESSURE IN mm.
mg. WATER PER GRAM CHARCOAL
200
400
600
800

FIG. 3

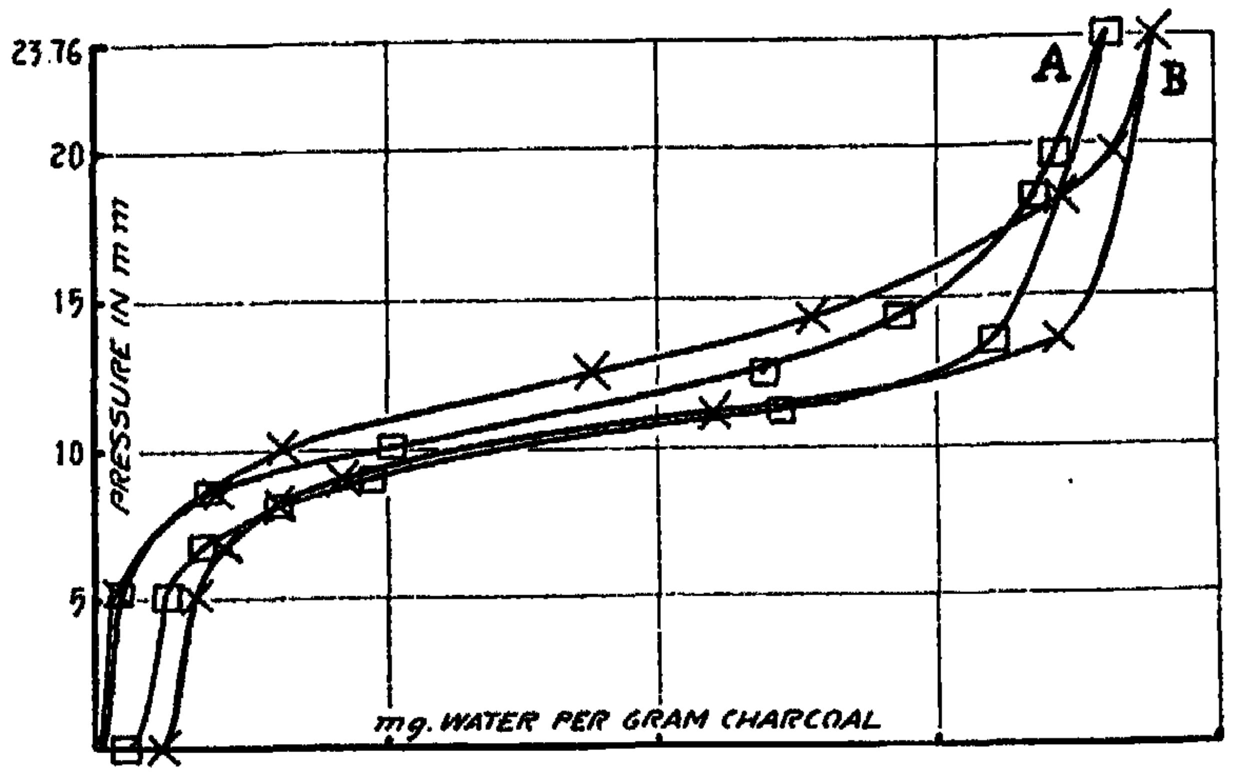
23.76
20
15
10
5
PRESSURE IN mm
mg. WATER PER GRAM CHARCOAL
A
B

FIG. 4

(c) *Charcoal B—evacuated at 170°C.*

(i) Outgassed for some time at 110°-120°. Temperature slowly raised to 270°-280°, and outgassing continued for 4 hours at this temperature.

(ii) 7.85 mg./gram.

(iii) 12.24 mg./gram.

(iv) 4.8 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2	2.1 mg./gram
O_2	2.7
CO_2	4.1
CO	0.6

(v) See Fig. 3.

(d) *Charcoal C—evacuated at 270°C.*

(i) Total time of outgassing 7½ hours, including 5¾ hours at 2400°-280°.

(ii) 11.14 mg./gram.

(iii) 9.83 mg./gram.

(iv) 2.8 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2	10.4 mg./gram
O_2	0.04
CO°	4.6
CO	2.6

(v) See Fig. 4A.

(e) *Charcoal C—evacuated at 800°C.*

(i) Eight hours' outgassing between 600°-800°, followed by 2½ hours between 780°-800°.

(ii) 14.53 mg./gram.

(iii) 22.70 mg./gram.

(iv) 7.1 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2	11.5 mg./gram
O_2	0.67
CO_2	11.3
CO	17.7

The final evacuation temperature was 800°.

(v) See Fig. 4B.

6. Discussion

In Table IV, certain of the data of the above experiments are tabulated together, all figures referring to milligrams sorbate per gram charcoal.

TABLE IV

	Charcoal A		Charcoal B	Charcoal C	
	Outgassed at 270°	Outgassed at 800°	Outgassed at 270°	Outgassed at 270°	Outgassed at 800°
Air sorption	11.66 (mean)	19.42	7.85	11.14	14.53
Saturation figure	308.3	393.3	810.4	360.0	376.0
Final dry air figure	25.1; 15.6	24.5	12.24	9.83	22.7

Attention at this stage will merely be drawn to some of the outstanding features of the results.

The first is that all the isothermals studied show considerable hysteresis similar to that found by previous workers. This is most marked for Charcoal B where, for example, the quantity of water held per gram at pressures of 14-15 mm. is about four to five times as much on the desorption as on the sorption isothermal, and where the maximum pressure difference between these two isothermals for the same *q* value is about 5 mm.

The next point is that the isothermals given by the different charcoals previously evacuated under practically identical conditons differ considerably from one another. Consider first the "270°C" charcoal isothermals. Whilst at low pressures, say up to 8-10 mm., there are no very pronounced differences apparent, each charcoal having the advantage, in the matter of specific absorptive power for water vapour, over a certain small pressure range, the curves become very different at higher pressures. Up to about 16 mm., Charcoal C absorbs most strongly. But between 16 and 18 mm. pressure, the capacity of Charcoal B is almost doubled and, from this point up to saturation, vastly exceeds the figures for the other charcoals. Of the two charcoals studied after evacuation at 800°, A is superior up to about 8 mm. pressure, is then passed by C throughout the whole intermediate pressure range, and finally passes it once more at a high P/p_0 ratio, finishing with a larger saturation figure. This last fact is closely connected with the general shape of the isothermals at high pressures. Those for B and C correspond to well-defined saturation limits, the curves becoming concave with respect to the pressure axis as p approaches p_0 (*c.f.* curves in Fig. 1 for a charcoal similar to B (Berl and Andress) and for sugar charcoal (Rakovsky)). Those for A, on the other hand, show an extra inflection, are convex to the pressure axis at high presure axis at high pressures, and exhibit a tendency to approach the p_0 value asymptotically (*c.f.* curves obtained by Katz, and by Rakovsky for blood charcoal and for coconut charcoal, presumably similar to C.)

Finally, the effects of temperature of outgassing appear definite. Charcoals outgassed at 800°, compared with those evacuated at 270°, show a bigger increase in weight on saturation with air, have a higher saturation value, show more marked hysteresis, and retain, or tend to retain, more water after passage of dry air at 25°. At low and intermediate pressures, the hysteretic loops for the "270°C." A and C charcoals practically entirely fall within those for the corresponding "800°C." charcoals.

The significance of these results will be discussed in a later paper.

University of London,
King's College,
April 17, 1929.

THE SORPTION OF WATER VAPOUR BY ACTIVATED CHARCOALS
PART III. ISOTHERMALS IN PRESENCE OF NITROGEN

BY A. J. ALLMAND AND P. G. T. HAND

1. Introductory

When considering the data set out in Part II.[1] of this series, it appeared possible that the oxygen present in the air stream might be exerting a specific effect on the results. For example, oxygen is slowly taken up by charcoal at room temperature in such a way that subsequent removal is only possible in the form of oxides of carbon. It was reasonable to suppose that the surface of the charcoal might thereby undergo such an alteration as to change its sorptive properties. Recent work of Rideal and Wright[2] and of Garner and McKie[3] would support this conclusion, as far as a true adsorption process is concerned, whilst Coolidge[4] definitely states that the presence of oxygen appears to alter the sorptive properties of charcoal. Against this is to be set the recent statement of Magnus and Roth[5] that two per cent of oxygen in the hydrogen used in investigating the sorption of hydrogen-carbon dioxide mixtures by charcoal out-gassed at 450° has no appreciable effect on the result. A second possibility was that oxygen has a specific effect in retarding the setting-up of sorption equilibrium, as Harned[6] had found the rate of sorption of chloropicrin to be retarded if the charcoal used contained oxygen. Such an effect, of course, would be anticipated to be small in comparison with the great retardation in sorption velocity naturally caused by the mere presence of *any* admixed gas.

To test these possibilities, we therefore carried out experiments on Charcoals A and C by a dynamic method in which the air stream was replaced by one of purified nitrogen (for experimental details, see Part I.[7]) It may be mentioned that, in both the experiments with Charcoal C, as also in that with Charcoal A, outgassed at 800°, the total time of passage of the moist nitrogen stream was between 1400-1500 hours for the complete sorption-desorption cycle. In the case of Charcoal A, outgassed at 270°, where the maximum water vapour pressure used was only 20.06 mm. (saturation value 23.76 mm.), this duration was only 430 hours. Assuming (see Part I.) that the proportion of oxygen by volume did not exceed $1:1 \cdot 4 \times 10^4$, and that the rate of passage of gas was 75-80 c.c. per minute, the *maximum* quantity of oxygen passed into the charcoal tube *in the course of a complete run* would be about 12 mg., i.e. 8-9 mg. per gram of charcoal, of which only a fraction would be absorbed.

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[1] J. Phys. Chem., **33**, 1151 (1929).

[2] J. Chem. Soc., **127**, 1347 (1925).

[3] J. Chem. Soc., **1927**, 2451.

[4] J. Am. Chem. Soc., **46**, 596 (1924).

[5] Z. anorg. Chem., **150**, 311 (1926).

[6] J. Am. Chem. Soc., **42**, 372 (1920).

[7] J. Phys. Chem., **32**, 452 (1928).

It should be added that, for the experiment with Charcoal C previously outgassed at 270°, a specimen was used which had been extracted by concentrated hydrochloric acid and in which the ash content had been reduced to some sixty per cent of that of the unextracted material.[1]

2. Rates of Sorption and Desorption

The actual lengths of time of passage of the moist nitrogen stream found necessary for the readjustment of equilibrium when passing from one point to another on the isothermals were much as in the air-stream experiments (extreme limits 8.5 and 241 hours). Expressing, as before, the rate of sorption or desorption by

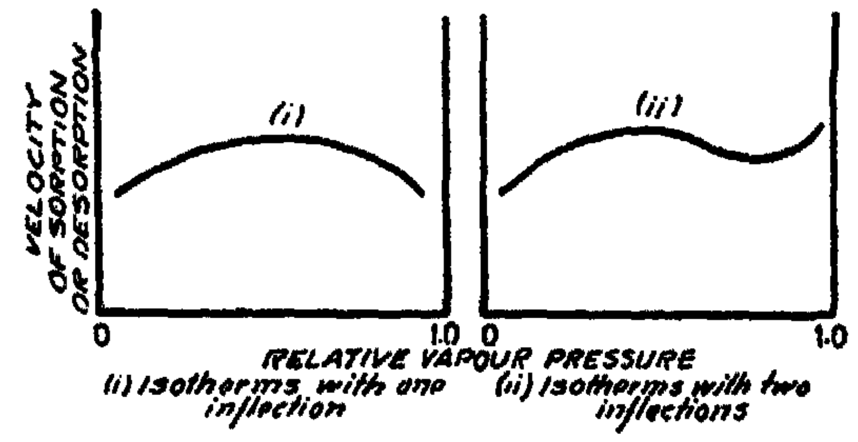

FIG. 1

$$\frac{\Delta w_1}{w_2 \times \Delta t \times \Delta p}$$

where Δw_1 is the loss or gain in water by a weight w_2 of charcoal in time Δt, and Δp is the difference between the initial and final equilibrium aqueous vapour pressures, precisely the same conclusions are drawn as from the air experiments, viz.

(i) Other conditions being similar, there is little difference between the charcoals employed, as also between charcoals outgassed at 270° and at 800°. Charcoal A (270°) however came to equilibrium more quickly than Charcoal A (800°).

(ii) the sorption process is more rapid than the desorption process at higher, and less rapid at lower, pressures.

(iii) there is a marked increase in the rate of sorption or desorption in the intermediate pressure range, as compared with the rates at immediately higher and lower pressures.

In addition, it was definitely shown that, in cases where the isothermal exhibits an inflexion at high pressures thereby tending to approach the saturation pressure asympotically), the velocity of sorption (or desorption) increases again as the pressures approach saturation. This had already been noticed in the air stream experiments in the only case in which data were available with such an isothermal. (Charcoal A outgassed at 800°). The

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[1] Part I, p. 453.

same behaviour was now found in the nitrogen stream experiments with both A and C charcoals outgassed at 800°. The point is one of interest, in that, like the regularity noted under (iii), it has a probable bearing on the structure of the charcoals. It may be added that Charcoal A outgassed at 270° also gives isothermals of this type, but that, in neither the air nor the nitrogen stream experiments, are the data available for seeing whether the velocity relations correspond. Diagrammatically, these velocity relations can be represented as in Fig. 1.

Finally, the velocities found in the nitrogen stream were quite similar to those obtained in the air stream—no systematic difference could be detected. Under the conditions of experiment, then, oxygen has no retarding effect on the processes concerned in the sorption of water vapour by charcoal, a result which accords with anticipation.

3. Results

An example of the results of a complete experiment using an air stream has been given in Part II. The course of an experiment using a nitrogen stream was very similar and there is no need to reproduce one *in extenso*. As in part II, our data will be presented in the form of isothermal diagrams (v), together with information on

(i) the outgassing process;

(ii) the sorptive power of the charcoal for dry nitrogen prior to the passage of the moist nitrogen stream;

(iii) the increase in weight after the final passage of the dry nitrogen stream (referred to the weight of the original evacuated charcoal);

(iv) the results of the subsequent evacuation of the charcoal.

(a) *Charcoal A—evacuated at 270°C.*

(i) A preliminary outgassing at room temperature, followed by three hours at 260°-270°.

(ii) 11.06 mg./gram.

(iii) 12.64 mg./gram.

(iv) 5.9 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2 9.3 mg./gram
O_2 0.5
CO_2 4.5
CO 0.07

(v) See Fig. 2A. It will be noticed that the aqueous vapour pressure was not pushed beyond 20.06 mm. (23.76 mm. is saturation pressure).

(b) *Charcoal A—evacuated at 800°C.*

(i) A preliminary outgassing at room temperature, followed by 3½ hours a 780°-800°.

(ii) 16.65 mg./gram.

(iii) 43.53 mg./gram.

(iv) 9.7 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2	10.1 mg./gram
O_2	0.07
CO_2	15.5
CO	8.3

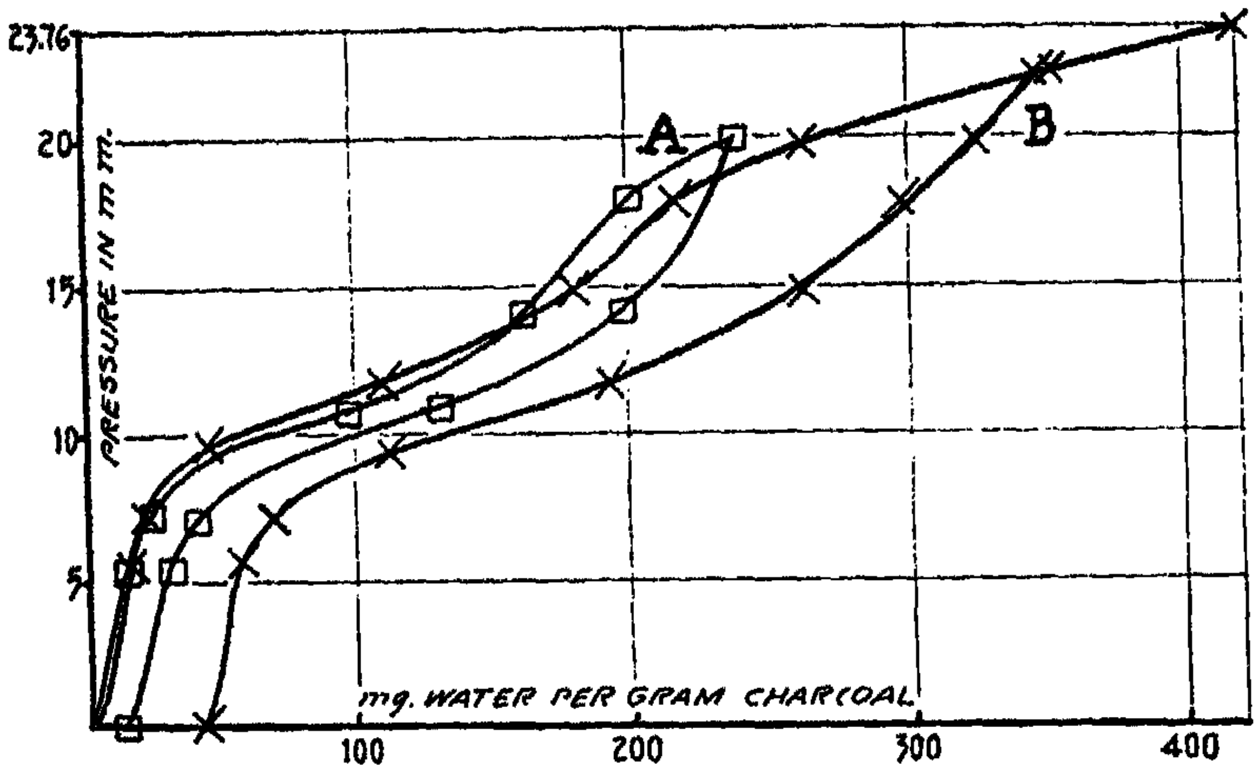

Fig. 2

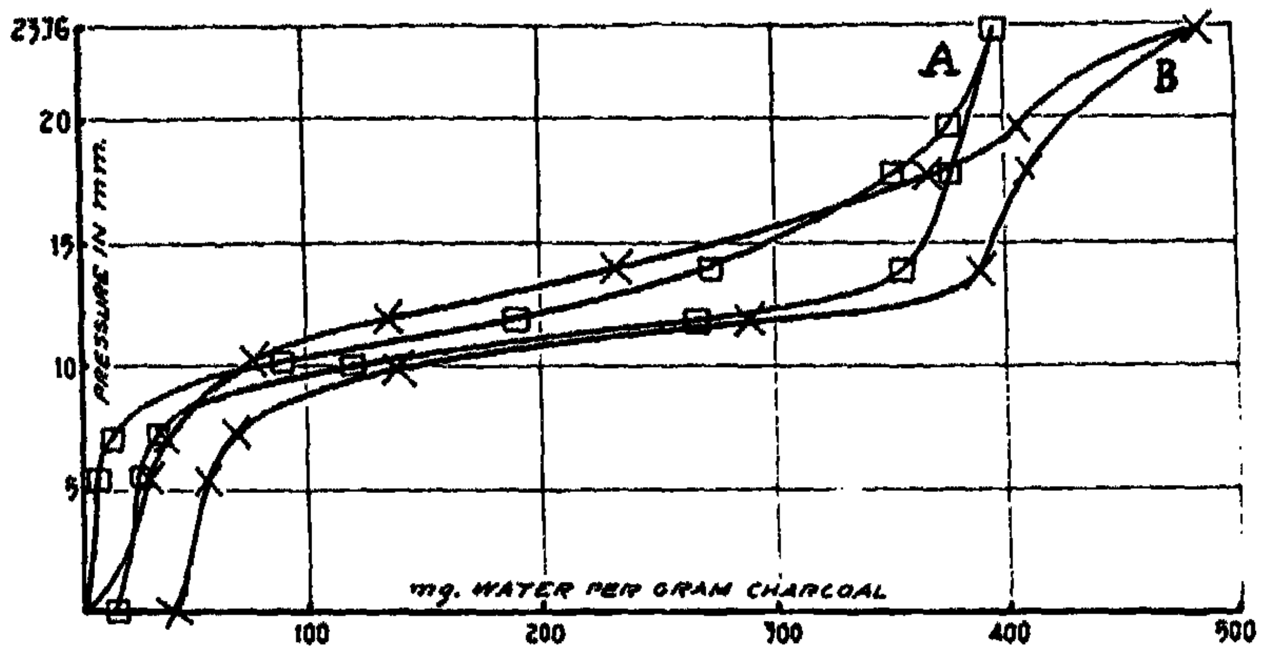

Fig. 3

The final evacuation temperature was 800°.

(v) See Fig. 2B.

(c) *Charcoal C—evacuated at 270°C.*

(i) Preliminary outgassing at room temperature, followed by five hours at 260°-270°.

(ii) 10.46 mg./gram.

(iii) 13.71 mg./gram.

(iv) 4.7 mg./gram of water recovered by evacuation at 270°.

The evolved gases amounted to

N_2	9.8 mg./gram
CO_2	3.5
CO	0.4

(v) See Fig. 3A.

(d) *Charcoal C—evacuated at 800°C.*

(i) Preliminary outgassing at room temperature, followed by 4½ hours at 780°-800°.

(ii) 22.68 mg./gram.

(iii) 40.02 mg./gram.

(iv) 9.2 mg./gram of water recovered by evacuation (90% of it at 270°, the residue at 800°, the final evacuation temperature). The evolved gases amounted to

N_2	9.9 mg./gram
CO_2	21.0
CO	9.5

(v) See Fig. 3B.

4. Discussion

In Table I, certain data obtained in the above experiments are collected together, all figures quoted representing mg. of sorbate per gram of sorbent.

TABLE I

	Charcoal A		Charcoal C	
	Outgassed at 270°	Outgassed at 800°	Outgassed at 270°	Outgassed at 800°
Nitrogen sorption	11.06	16.65	10.46	22.68
Saturation figure	——	419.3	394.5	483.6
Final dry nitrogen figure	12.64	43.53	13.71	40.02

The isothermals, on the whole, resemble those described in Part II, although there are differences in detail. There is again considerable hysteresis, of about the same magnitude as observed previously. (Charcoal B, which in the air-stream experiments, showed this phenomenon to the greatest extent, was not worked on in nitrogen.) The air and nitrogen curves for Charcoal A are very similar both for "270° C." and for "800°C." charcoals, and it is reasonable to imagine that if the full pressure range had been worked over with the "270° C." charcoal in nitrogen, the similarity would have been still more marked, particularly in the low-pressure regions of the desorption curves. The increased amount of water held at "zero" water vapour pressure by the "800°C." charcoal in the nitrogen stream as compared with the air-stream experiment is undoubtedly closely connected with the increased saturation figure.

In the case of Charcoal C, the "270°C." isothermals in air and in nitrogen are again very similar. But this is not so with the "800°C." charcoals, except over the range of intermediate pressures. Both at lower and at higher pressures, considerably more water vapour has been taken up in the nitrogen experiment; and indeed, to such an extent that, at pressures near saturation, the isothermal is convex to the pressure axis, as is always the case for Charcoal A.

The general effects of a higher outgassing temperature are, in all respects, as found for the air-stream isothermals and, in fact, are even more marked.

A fuller discussion is reserved for a later paper.

University of London,
King's College,
April 17, 1929.

THE ADSORPTION OF SULPHUR DIOXIDE BY PLATINISED ASBESTOS

BY D. O. SHIELS

Introduction

Apparently no work has been published within recent years on the adsorption of sulphur dioxide by platinum catalysts, and it seemed worth while to investigate the subject in view of the use of platinum catalysts in the formation of sulphur trioxide.

It was intended to investigate the adsorption at a number of different temperatures, and if the process was reversible to calculate the heat of adsorption, and also to determine the effect of catalytic "poisons" such as arsine on the adsorption.

For reasons which will appear later the adsorption has been determined only at one temperature, and the effect of poisons has not yet been investigated. Apparently the only other investigations on the actual adsorption of sulphur dioxide by platinum is that of Mond, Ramsay, and Shields, although a large amount of work has been done on the catalytic effect of Pt on the oxidation of sulphur dioxide to sulphur trioxide.

In the above investigation[1] no isotherm was determined. It was found that one vol. of platinum black adsorbed 84.2 volumes of sulphur dioxide at atmospheric pressure, and that only one-fifth of the adsorbed sulphur dioxide could be removed at room temperature in vacuum. In order to remove the gas completely, the platinum black had to be heated to a red heat which process converted the platinum black to platinum sponge.

Experimental

Method of determining Sorption.

The method of the experiment was to expose the solid sorbent after preliminary heating and evacuation to a known volume of sulphur dioxide at known pressure and temperature and to measure the equilibrium pressure. The final volume being also known the amount of gas sorbed could be readily calculated.

Preparation of Platinised Asbestos.

The asbestos used was British Drug House brand specially prepared for use in Gooch crucibles. It was boiled in a solution of sodium formate and then a 5% solution of platinic chloride previously neutralized with a pure sodium carbonate was added. The mixture was then boiled. After the platinum had deposited, the platinised asbestos was filtered then washed with 10% sulphuric acid, hot distilled water, hot 5% hydrochloric, then with hot distilled water until free from chloride and sulphate.

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[1] Z. physik. Chem., 25, 667 (1898).

The platinised asbestos was then dried in the air oven at 110° C placed in the container C. The weight of the asbestos used was 0 952 grms and the final weight of the platinised asbestos 1.488 grms giving a weight of 0.536 grms of platinum.

Description of Apparatus.

The apparatus used was similar to that shown in Fig. 1. The platinised asbestos (1.488 grams containing 0.536 grams of platinum) was contained in the glass vessel C (See Fig. 1) which was connected by a mercury-sealed ground joint to the gas reservoir R, which was connected with the manometer M_1 of 2mm tubing, a McLeod gauge C, two drying tubes containing Merck's phosphorus pentoxide, which was not further purified, a tube L containing soda-line, and through tap T_7 to an iron three-stage mercury vapor diffusion pump backed by a water-pump. The container C and the reservoir R were immersed in the water of a thermostat to the level of the dotted line. Through T_3 R could be put into communication with the apparatus for supplying pure sulphur dioxide, which was prepared as follows:—

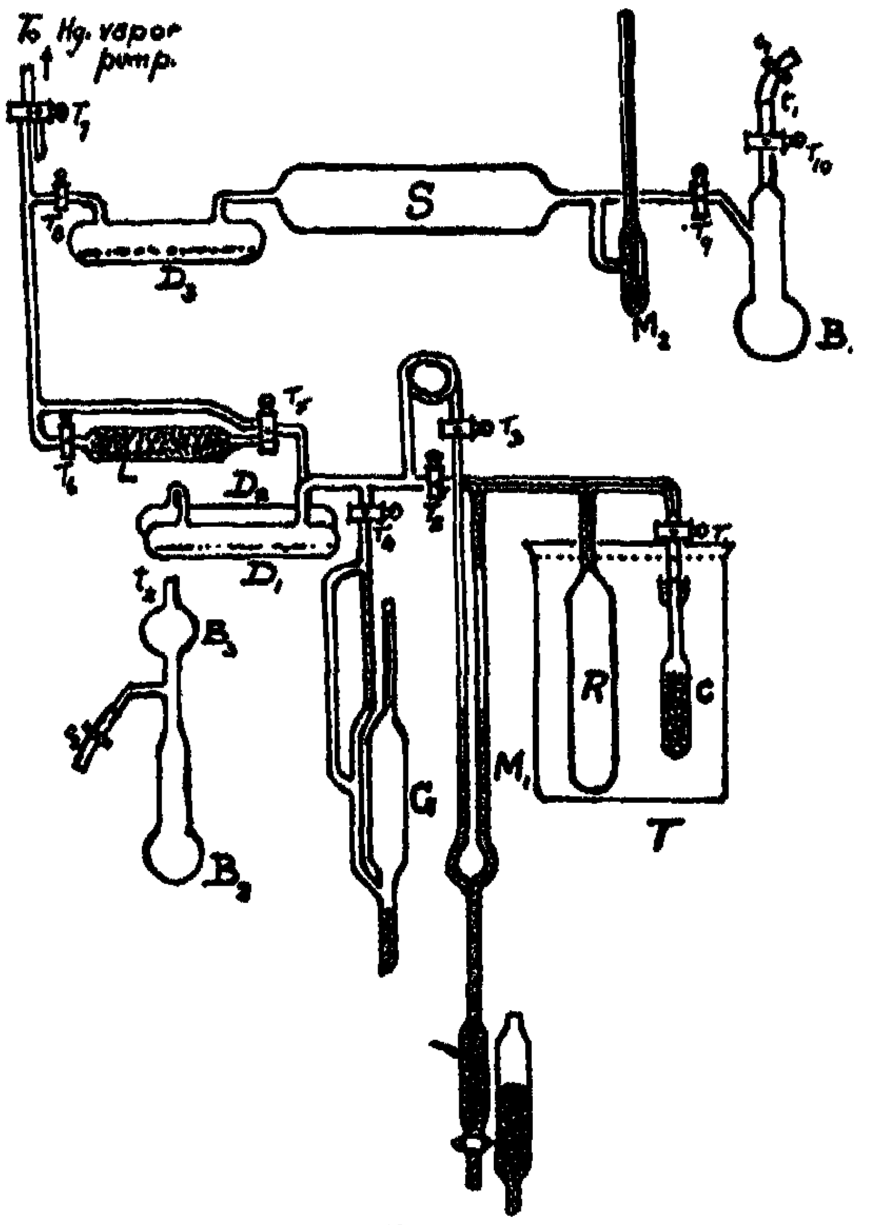

Fig. 1

Preparation of Pure Sulphur Dioxide.

The screw clip C_1 on the rubber tubing attached to the tube t_1 was closed and T_{10}, T_9, T_8 opened through to the mercury pump. After evacuation to a pressure of 2mms or less the tap T_{10} was closed. This procedure was adopted in order to evacuate the bore of the Tap T_{10}.

The parts B_1, S and D_3 were then evacuated to $1-2 \times 10^{-3}$ mm pressure.

The bulb B_2 was partly filled with a solution of pure (A.R.) sodium sulphite and t_2 inserted in the rubber pressure tubing attached to t_1. By means of the side arm attached to B_2 the solution was boiled under a vacuum in order to remove dissolved air. The screw clip C_2 was then closed. B_2 was then raised to a vertical position above B_1 and the sodium sulphite solution run into B_1, care being taken to leave some solution above the tap T_{10}, thus preventing the ingress to B_1 of any air from the bulb B_2 which may have diffused through the pressure tubing.

The bulb B_2 was then detached and cleaned, and the liquid in the tube t_1 removed.

Bulb B_1 was then partly filled with a dilute solution of pure (A.R.) sulphuric acid, and a similar procedure gone through, with the following modification.[1] As soon as the acid reached the sodium sulphite solution the sulphur dioxide evolved would prevent the remainder of the solution running down. It was therefore necessary to have a higher pressure above the acid solution in B_3. Benzene in which the solubility of air is very small was carefully run onto the surface of the liquid in B_3, through the rubber connection. Air was then slowly admitted by means of the screw clip c_2 into the bulb B_2.

In this way the liquid was forced into B_1 against the pressure of SO_2. As before the tap T_{10} was closed while some of the solution remained in C_1. In this way no air or benzene was admitted to the bulb B_1.

S was a glass tube of about 400 ccs. capacity which acted as a reservoir for the SO_2. D_3 was a drying tube containing phosphorus pentoxide, M_2 a manometer to indicate the pressure of the gas in S. After S had been partly filled with sulphur dioxide the tap T_9 was shut off.

A supply of pure dry SO_2 was thus obtained. All taps were lubricated with a fairly stiff Ramsay grease.

Preliminary Evacuation.

A small electric furnace was placed around the container C which with its contents was evacuated and heated to 370°C.

The furnace was then removed and a thermostat T raised into position. The temperature was kept constant to 0.03°C. The stirrer, thermo-regulator, and heating apparatus are not shown in the diagram.

Measurement of Adsorption.

The volume of C up to the top of the tap T_1 had previously been determined, and also the volume of R from top of tap T_1 to a mark on the right arm of the manometer. The volume per cm length of the manometer tube had also been determined.

After the evacuation was completed tap T_1 was shut, and pure dry sulphur dioxide admitted to R.

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[1] Hand: J. Chem. Soc., 123, 2576 (1923).

After temperature equilibrium had been reached the pressure was determined to 0.01 mm of mercury by means of a travelling microscope. The gas was then admitted to C and the pressures read at intervals until constancy to 0.01 mm was obtained for a 20 minute interval.

The adsorption was rapid the pressure usually falling to nearly the equilibrium valve in the first 20 minutes.

Allowance was made for the volume occupied by the platinised asbestos, this being calculated from the weights of platinum and asbestos.

The initial pressures in C and R being known and the final pressure in C and R, the volume of gas adsorbed by the platinised asbestos could be readily calculated. Blank experiments were carried out with a sample of the same kind of asbestos but un-platinised. The results for unplatinised and platinised asbestos are shown in Tables II and III respectively, the results in the latter case being calculated in the assumption that sorption is due to the asbestos alone. The results have also been calculated on the assumption that in the case of platinised asbestos the whole of the sorption is due to the platinum. These results are tabulated in Table I.

Table I

Platinum

Pres. of gas at equilibrium in Mm mercury P	CCs. of gas adsorbed (25°, 760 mm	CCs. at N.T.P. per gram of Platinum observed q	 calculated q
Run (4)			
1.85	0.037	0.063	
4.93	0.093	0.159	
7.98	0.128	0.219	
		a =	0.1154
		b =	42.32
Run (5)			
5.59	0.094	0.161	0.166
8.59	0.125	0.214	0.211
17.70	0.163	0.278	0.284
27.09	0.189	0.323	0.321
38.90	0.205	0.351	0.347
29.54	0.192	0.327	0.327
13.98	0.144	0.246	0.261
6.68	0.109	0.185	0.184
2.93	0.064	0.110	0.108
0.63	0.022	0.038	0.029
Run (6)			
2.96	0.063	0.108	

For curve see Fig. 2 no. 3.

The results of run (5) are plotted in Fig. 2. The following shows the preliminary treatment of the platinised asbestos before each run. Several runs were made before the tendency of the mercury in the manometer to stick was overcome. Although the mercury had been twice distilled and the manometer cleaned very thoroughly with strong chromic acid there was a tendency to stick which made the pressure readings at low pressures unreliable. This was overcome by adding the extension to the bottom of the manometer and moving the surfaces simultaneously by means of the reservoir, gradually decreasing the amplitude of the movement.

Run (4). Run (4) was then made. The platinised asbestos was evacuated to 1.3×10^{-3} mm at room temperature and then heated for 2 hrs. at 370°C

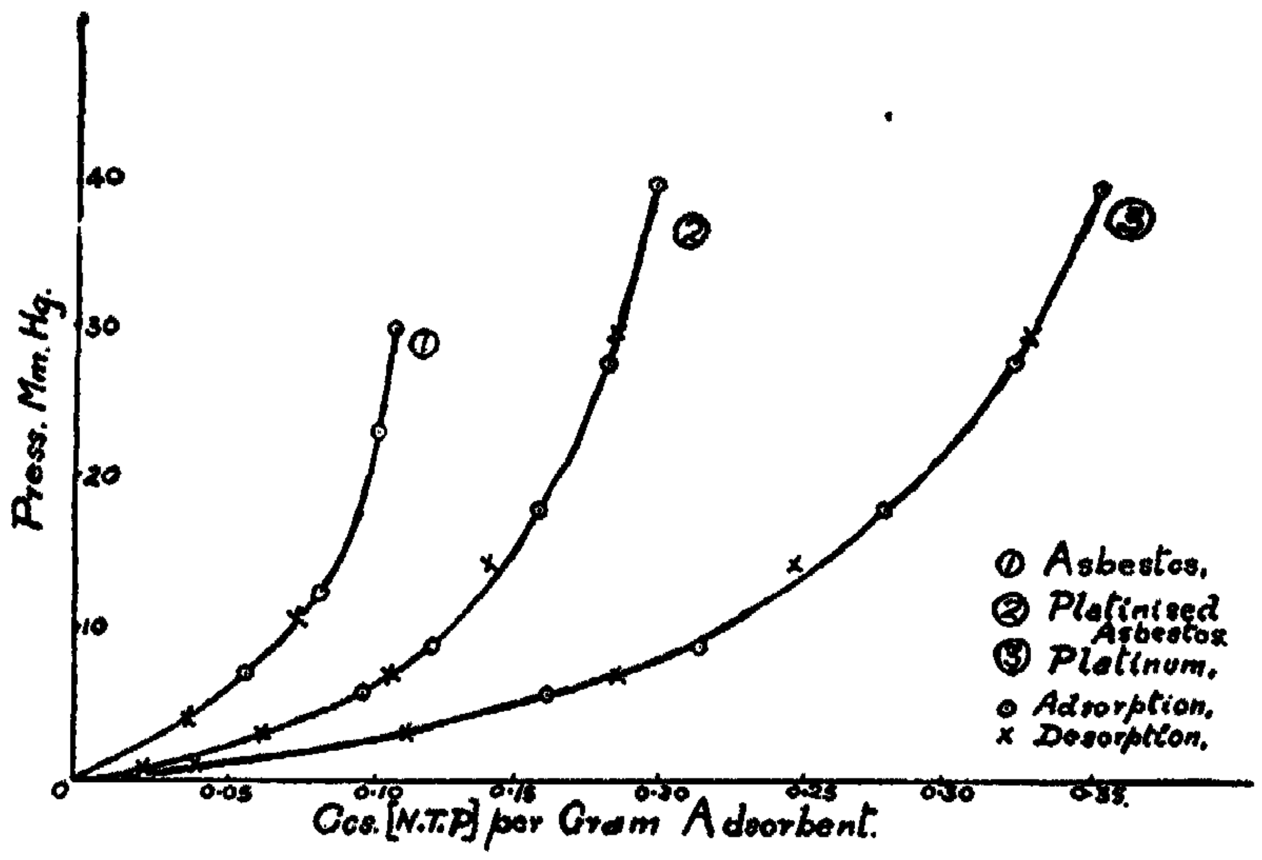

FIG. 2

the pressure being 1.7×10^{-3}. The volume of gas evolved at the end of this period was 0.0007 ccs in 10 minutes. The readings shown in the table were then obtained.

Run (5). After desorption in Run (4) the mass was evacuated to a low pressure for half an hour at room temperature and then for 1½ hours at 370° at pressure of 2×10^{-3} mm.

The volume of gas evolved at end of this period was 0.005 ccs in 20 minutes. The readings for run (5) in the table were then obtained.

Run (6). After desorption in run (5) the mass was evacuated at 25°C for 15 minutes at 6×10^{-3} mm pressure at the same temperature. The reading shown in Table II was then obtained.

The asbestos which weighed 1.016 grams was placed in the container C and the whole evacuated to 3.3×10^{-3} mm pressure in the cold, and then heated for 40 minutes to 370°C with the pump running. The final pressure was 2.6 × 10^{-3} mm and the volume of gas given off during the last 10 minutes at the above temperature was 0.0003 cc.

Sorption was then carried out in the usual way, and desorption to 3.95 mm pressure.

TABLE II

Unplatinised Asbestos

	P	q observed	q calculated
1	6.975	0.055	0.055
2	12.17	0.079	0.076
3	22.76	0.0995	0.0995
4	29.63	0.104	0.108
5	3.95	0.036	0.037
6	10.526	0.071	0.071
a =	0.08125		
b =	15.32		

The asbestos was then pumped out to 9 × 10^{-4} mm pressure at 25°C and then point (6) was determined.

TABLE III

Platinised Asbestos

wt. of Platinum = 0.536 grms.
wt. of Asbestos = 0.952 grms.
q = ccs of gas at N.T.P. per grm of asbestos

p	q	p	q
5.59 mm	0.0904	29.54	0.1848
8.59	0.1203	13.98	0.1386
17.70	0.157	6.68	0.1048
27.09	0.182	2.96	0.0615
38.90	0.1973	0.63	0.0212

Details of treatment same as in case of Table I. For curves corresponding to Tables II and III see Fig. 2, nos. 1 and 2.

Reproducibility of Results.

The points shown in Table I under runs (4) and (5) and (6) all live very closely on the same curve.

There may however be a very slight tendency for the successive heat treatments to decrease the sorptive capacity. A slight change in color of the platinised asbestos was noticed after several heatings.

The details of the experiments on unplatinised asbestos indicate also that the results are closely reproducible, point (6) being obtained after pumping out at 25°C and then again exposing to sulphur dioxide.

Discussion of Results.

It will be seen that the sorption by the platinised asbestos is very much greater than that due to the asbestos alone.

It is not possible to determine the amount sorbed by the platinum alone, by difference, since the asbestos surface in the platinised asbestos is more or less completely covered by the finely divided platinum.

Thus the sorption by the platinised asbestos may be due to sorption both on platinum and on asbestos, and it is not possible to determine the separate effects quantitatively. It is clear, however, that there is definite sorption by the platinum.

In the above cases the sorption is reversible, and there is a complete absence of any hysteresis. Pollard[1] has shown that in the sorption of carbon monoxide, and hydrogen by platinised asbestos hysteresis occurred. The explanation given by Pollard is that although the gases were cooled in liquid air, some impurities from the stop-cocks were not completely removed and inhibited the sorption to a certain extent, although the adsorbed impurity did not strongly influence the desorption.

By allowing sufficient time both the gases could be completely removed by pumping out at 0°C.

In the author's experiments on SO_2 although no special precautions were taken to remove possible impurities from the stop-cock grease (no liquid air being available) the sorption process was completely reversible.

The quantity sorbed is considerably less than in the case of Pollard's experiments. He found in the case of carbon monoxide that 40 vols. of gas were sorbed per vol. of platinum at a pressure of 20 mm whereas in the above experiments on sulphur dioxide a more readily condensible gas the quantity sorbed at the same pressure was only 11.6 vols per vol. of platinum.

The isotherm at 25°C is represented quite accurately by Langmuir's equation $q = \frac{abp}{1 + ap}$ where q is the quantity of gas sorbed per gram of sorbent, p is the equilibrium pressure in mm of mercury and "a" and "b" are constants.

This applies both for platinised and unplatinised asbestos the constants being different.

The observed and calculated values are shown in Tables I and II. The agreement is quite good.

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[1] J. Phys. Chem., 27, 356 (1923).

[2] J. Phys. Chem., 40, 1368 (1918).

Summary

The sorption of sulphur dioxide by platinised asbestos has been studied in absence of air at 25°C and up to 40 mm pressure.

It is reversible, there being no evidence of hysteresis.

The isotherm is represented quite accurately by Langmuir's equation

$$q = \frac{abp}{1\ ap}$$

The above work was carried out in the Physics Department of the University of Tasmania and the Author's thanks are due to Prof. McAuley for facilities placed at his disposal.

Owing to the Author's removal, further work at other temperatures and on the effect of poisons could not be carried out.

University of Tasmania,
Hobart,
Feb. 12, 1929.

THE ADSORPTION OF SULPHUR DIOXIDE BY PLATINUM BLACK

BY D. O. SHIELS

2155

Introduction

Previous work[1] on the adsorption of sulphur dioxide by platinised asbestos had shown that the process was a reversible one. The adsorption was small relatively to that of carbon, and of hydrogen by platinised asbestos as found by Pollard.[2]

In many cases of adsorption of gases by solid adsorbents the more easily condensible the gas is the greater is the adsorption, but there are numerous exceptions to this. Pollard has shown that carbon monoxide is able to displace adsorbed hydrogen from platinised asbestos. There are many other example of the highly specific nature of the adsorption process.

There are numerous reasons which might be adduced for the relatively small amounts of sulphur dioxide adsorbed, such as the specific nature of the process, the difference in structure of the catalysts prepared in different ways, the possible "poisoning" of the adsorbent by traces of vapours from the tap grease, or by impurities in the sulphur dioxide due to the fact that the Merck's phosphorus pentoxide had not been further purified. In addition the interpretation of the results is rendered difficult by the presence of the asbestos, which itself, as was expected, showed definite though small adsorption of the sulphur dioxide. It was decided, therefore, to carry out experiments with platinum black.

An attempt was made to dispense with the use of grease on the taps T_0 and T_1 interposing between T_1 and T_2 a U tube containing activated carbon which could be cooled in liquid air or by solid carbon dioxide. Some preliminary trials with metaphosphoric acid as a lubricant seemed promising. The lubricant was prepared by the method of Chapman and Gee[3] Stick phosphoric acid was washed with distilled water to remove the crystals which coat the surface, and then placed in a desiccator until the surface layers had the right consistency. The taps were then lubricated with this, and the upper rims coated with melted Ramsay grease to protect the lubricant from the moisture of the air. In this way it was possible to maintain a high vacuum in C and R for several days, the taps remaining satisfactorily turnable.

It was decided to proceed in this way. But on repeating the process after placing the platinum in position both taps stuck fast. It was obviously useless to attempt an extended series of experiments under such conditions of uncertainty as to the reliability of the apparatus and it was finally decided to carry out the work in the same way as in the previous work on platinised asbestos.

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[1] J. Phys. Chem., 33, 1167 (1928).

[2] J. Phys. Chem., 27, 356 (1923).

[3] J. Chem. Soc., 99, 1726 (1911).

Apparatus

The apparatus used is shown in Fig. 1. The platinum black was contained in the bulb C which was connected by the end-on tap T_c to the gas reservoir R. R could be isolated from the rest of the apparatus by the end-on tap T_1 (shown in Fig. (1) as a mercury seal tap for simplicity in drawing) R was connected by a capillary tube to the mercury manometer M. The rest of the apparatus was similar to that described in the previous paper and the method of using it was the same.

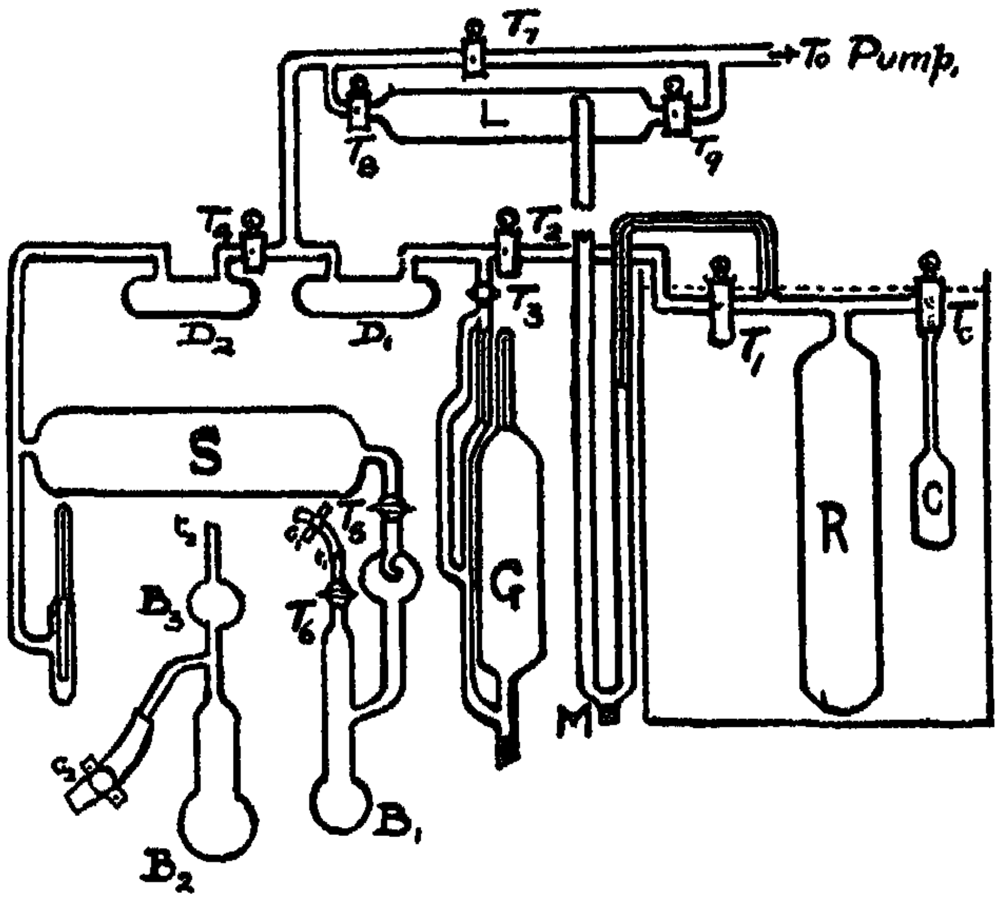

Fig. 1

A thermostat could be raised into position around R and C, the water level being adjusted to the position indicated by the dotted line. Thus the whole of the essential parts of the apparatus with the exception of the very small volume represented by the capillary tube, were kept beneath the surface of the water. The volume of C was determined from the weight of water it contained. That of R was determined by filling C with dry air at known temperature and pressure and allowing it to expand into the previously evacuated reservoir R and measuring the final pressure in C and R, the temperature being known. The volume of C was 18.219 ccs and that of R was 74.70 ccs. With the exception of the temporary rubber connection between B_3 and T_6 used in introducing the solutions the whole of the apparatus was fused together.

The pumping system consisted of a Kraus-type glass mercury vapour pump backed by an iron two-stage Langmuir mercury vapour pump which was backed by a Cenco Hyvac rotary oil pump. The pressures in the manometer were read by a cathetometer to 0.02 mm. The temperature of the water in the thermostat was maintained at 25°C ± 0.025°C.

Materials

All glass parts were thoroughly cleaned with chromic acid, or by successive treatments with chromic acid, and alcoholic potash solutions, and then distilled water. The rubber tubing attached to the manometer M and the McLeod gauge G and the short pieces used in connection with the bulb B were boiled with caustic soda solution, distilled water, dilute nitric acid and finally washed acid free and dried by current of air.

Preparation of Platinum Black.

The platinum black was prepared from a platinum crucible by solution in aqua regia. The solution was evaporated nearly to dryness to remove excess acid, and then taken up with distilled water until concentration was about 3%. It was then neutralized with pure solid sodium carbonate. Sodium formate solution containing 44 grms in 100 ccs of water was boiled and the platinic chloride solution added gradually.

The precipitated platinum black was filtered and washed free from chloride. It was then dried in the air oven at 110°C. It was introduced into C through a filter funnel, all lubricant having been carefully removed from the tap T_c, the end of funnel passing well below the tap barrel so that there was no contamination by any trace of tap grease which may have been left. The weight of the platinum black used was 4.545 grams.

Sulphur Dioxide.

This was prepared as described in the previous paper from pure A.R. B.D.H. sodium sulphite, and sulphuric acid.

Phosphorus Pentoxide.

Schuchardt's phosphoric pentoxide was heated in glass tubes to 200°C and a current of ozone passed through it for two hours. The tubes were then sealed until the substance was required. It was then quickly transferred to the tubes D_1 and D_2 and these sealed in place.

Mercury.

The mercury was purified by agitation with dilute nitric acid saturated with mercurous nitrate, and then carefully dired. The mercury in the reservoirs attached to manometer and McLeod gauge was protected from the atmosphere by soda lime tubes which were kept closed, except during the raising or lowering of the reservoirs.

Results

Blank experiments were done in order to determine the adsorption of the sulphur dioxide on the walls of the container C before introducing the platinum black. The quantities so absorbed were very small and have been neglected in making the calculation of the adsorption by the platinum black. Table I shows the results of these blank experiments. The results are plotted in Fig. 2.

TABLE I

Temp. = 25°±0.025°C

Press. in cm. Mercury	ccs. N.T.P. adsorbed	
2.78	0.0060	(6)
3.24	0.0068	(7)
5.46	0.0098	(10)
6.50	0.0108	(11)
10.51	0.0138	(14)

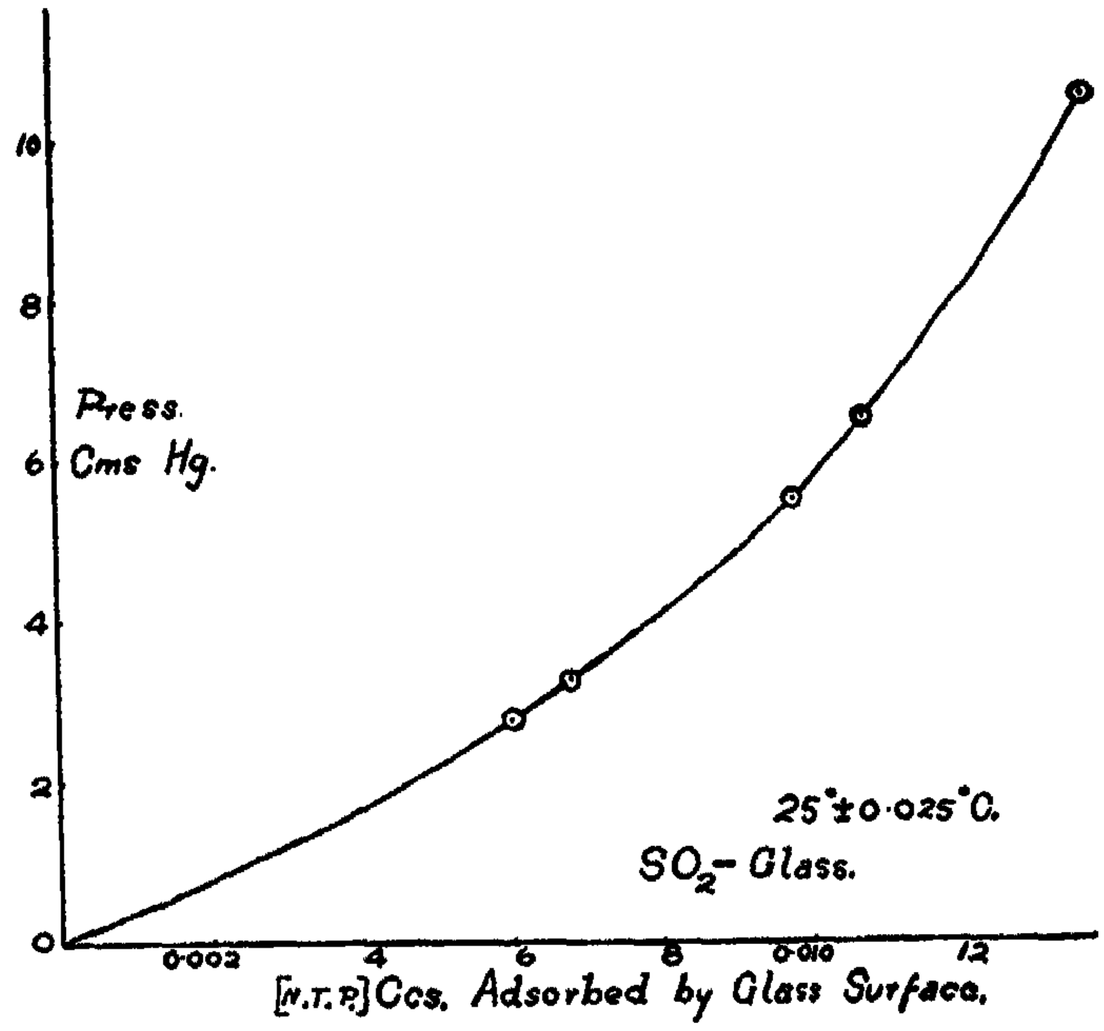

FIG. 2

No great accuracy is claimed for these figures as the experimental error is possibly of the order of 0.0009 ccs but they show the approximate magnitude of the adsorption on the glass surface at these somewhat low pressures.

Assuming that the diameter of the sulphur dioxide molecule is 4.84×10^{-8} cms and taking the quantity adsorbed as 0.01 ccs at pressure of 5.7 cms the total area occupied by the molecules in this volume of gas will be 627.6 $cm.^2$ The area of the internal surface of the container was 65 cm^2, giving the number of layers 9.65.

Evans and George[1] have calculated from the results of Mülfarth[2] that sulphur dioxide on glass gave layers 32 molecules thick at atmospheric pressure. For carbon dioxide they found layers approximately 5 molecules thick at pressure of 121 mm and presumably at 0°C.

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

[2] Ann. Physik, (4) 3, 328 (1900).

Preliminary Treatment of Platinum Black

The container C was evacuated at room temperature for 5 hours including 2½ hours at 80°C the pressure at the end of this period being 5 × 10^{-4} mm. The temperature was then raised to 230°C and the evacuation continued for 2 hours. The final pressure at this temperature was 9 × 10 mm. Higher temperatures were not used for fear of altering the platinum black.

The sorption experiments were then carried out after cooling the container C and adjusting the thermostat. It was considered that equilibrium had been attained when the pressure in R and C remained constant to 0.02 mm for a twenty minute interval. Table II shows the results obtained with platinum black.

TABLE II

	Press. in cms. Mercury	Ccs. at N.T.P. adsorbed per gram platinum	Vol. SO_2 at N.P.T. adsorbed per vol. of platinum
1	0.00	0.398	7.95
2	0.00	1.473	29.46
3	0.704	2.59	51.8
4	7.348	3.857	77.14
5	17.404	4.214	84.28
6	4.851	3.852	77.04
7	1.693	3.667	73.34
8	0.740	3.567	71.34
9	0.00	3.180	63.60
10	0.00	2.702	54.04
Second Adsorption			
11	2.637	3.131	62.62
12	5.432	3.280	65.60
Second Desorption			
13	1.534	3.167	63.34
14	0.562	3.104	62.08

Point (9) was obtained by exposure to charcoal cooled in solid carbon dioxide, the apparatus being arranged as in Fig. 3.

The charcoal was heated for 2 hours and evacuated to 2.6 × 10^{-3} mm at 250°C and when cold the pressure was 2.2 × 10^{-4} mm. The charcoal tube was then removed and weighed against a counterpoise of approximately the same weight and external volume. After replacing the charcoal tube the leads up to T_1 were evacuated to 3 × 10^{-3} mm.

Sulphur dioxide was then let in to this part to a pressure of several cms., and the evacuation repeated to 5 × 10^{-4} mm. This was done in order to wash out any traces of air from this part of the apparatus. T_1 was then opened through to R and the evacuation of the reservoir continued down to

5×10^{-4} mm. The charcoal was cooled by placing solid carbon dioxide round the container. T_2 was then shut and T_c opened. The pressure rose to a few mms. in R. The tap to the charcoal was then opened and the pressure immediately fell to zero.

The charcoal tube was left in connection with the container C for 2 hours. The necessary taps were then shut, and the charcoal tube removed and weighed, and the amount of gas desorbed calculated. As the amount recovered in this way was not very great, the platinum was heated to 250° in order to find out whether the adsorbed sulphur dioxide could be recovered at this temperature.

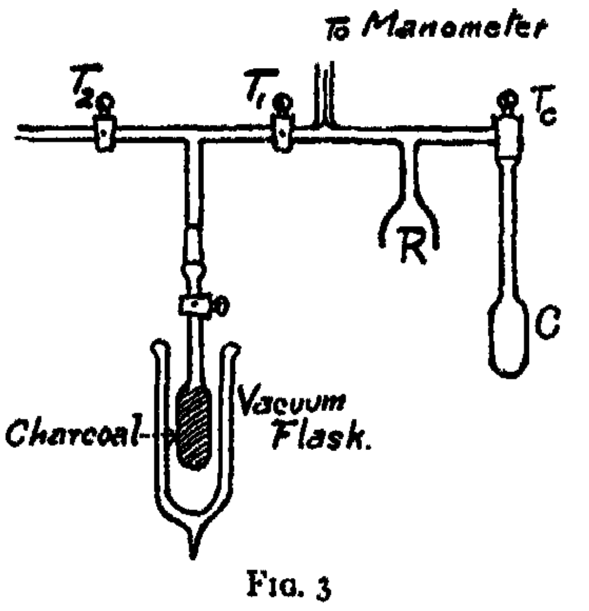

Fig. 3

After 4 hours 50 minutes heating to 250° the platinum black being exposed to the low pressure of sulphur dioxide developed by this process, and an additional 3½ hours at the same temperature the platinum being exposed to the charcoal cooled in solid carbon dioxide there still remained 2.95 ccs of sulphur dioxide adsorbed per gram of platinum. Point (10), a second adsorption was then carried out up to a pressure of 5.432 cms and a second desorption to 0.562 cm. Points (11) to (13).

The results shown in Table II are plotted in Fig. 4.

Discussion of Results

In striking contrast to the results obtained with platinised asbestos the process in the case of platinum black is not a reversible one. There appears to be a strong irreversible adsorption, and in addition a weaker more nearly reversible adsorption which however shows some hysteresis.

Ramsay and Shields showed that 1 vol. of platinum black adsorbed 84.2 vols. of sulphur dioxide at 1 atmosphere pressure and that only one-fifth of this could be recovered by evacuation at room temperature. In the case of the present experiments 84 vols. of gas were adsorbed per volume of platinum black (assuming density = 20) at 17.4 cms pressure, and only 20.6 volumes could be recovered by prolonged evacuation at 25°C.

Pollard[1] found that there was hysteresis in the adsorption of carbon monoxide and of hydrogen by platinised asbestos. His explanation was that traces of vapour from the tap lubricant adsorbed by the platinised asbestos inhibited the adsorption of the gases, but did not prevent the removal of the adsorbed gases.

If this explanation be correct then one would expect the second adsorption curve to follow the same course as the first. In the author's experiments this

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[1] J. Phys. Chem., 27, 356 (1923).

was not so. The second adsorption curve follows a course parallel to the desorption curve not to the first adsorption curve.

An explanation of hysteresis frequently given especially in case of porous adsorbents is that traces of less readily condensible gases remain on the solid sorbent even after evacuation at fairly high temperatures. These are displaced by the more readily condensible adsorbate giving a total pressure as read by a manometer higher than that which should correspond to the quantity of adsorbate held by the solid, since it is made up of the pressure of the adsorbate gas corresponding to the quantity of adsorbate held, plus the pressure due to the displaced less condensible gas.

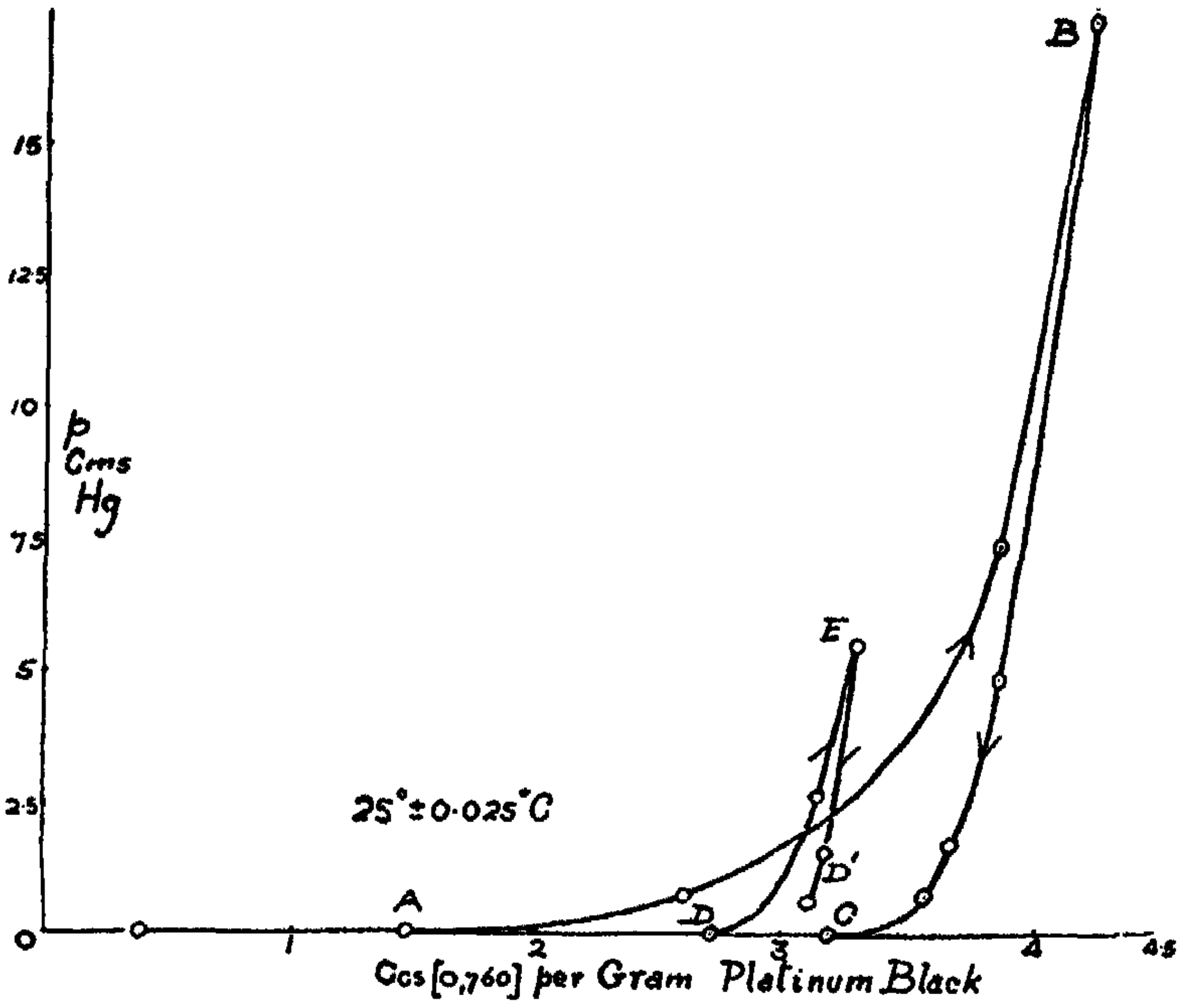

FIG. 4

It is not likely that such an explanation could hold in the present case since the isotherm in its first stages shows zero pressure for a very considerable quantity of gas adsorbed. It is unlikely that certain highly active centres of the platinum black adsorb sulphur dioxide very strongly, but do not adsorb other less readily condensible gases such as oxygen or nitrogen *at all*, and that there are other less active centres which adsorb these gases, and from which they can be displaced by the sulphur dioxide. Some such mechanism would be necessary for the above explanation to hold.

It seems more likely that the adsorbed sulphur dioxide is oxidised to sulphur trioxide at certain active centres of the surfaces (the difficulty of completely removing oxygen from platinum is well known). This part of the curve is represented by OA.

AB represents the adsorption of sulphur dioxide on less active centres with displacement of other gases. BC represents more nearly the true adsorption-desorption curve. DE is approximately parallel to BC but this second adsorption curve DED′ also shows some hysteresis, although not to the same extent as the first curve ABC. The shift of the curve DE to the left of CB may be due to the prolonged heating (8½ hours to 250°C) diminishing the adsorptive capacity of the platinum black.

Again, it is possible that the highly active centres which adsorb the oxygen which is so difficult to remove also adsorb sulphur dioxide very strongly and that these two kinds of molecules are held contiguously but do not react at low temperatures. These centres being saturated (OA) further addition of sulphur dioxide displaces other gases, (from less active centres) (AB) thus on desorption giving a hysteresis loop, ABC. On raising the temperature to 250°C the adsorbed oxygen and sulphur dioxide react to form sulphur trioxide. This is adsorbed from the vapor state on other surfaces of the platinum black and reduces the total capacity for adsorbing sulphur dioxide. Hence the shift of the curve DE to left of CB.

The difference in the reversibility of the curves in case of platinum black and platinised asbestos is not readily explicable. A supported catalyst is not usually less active than an unsupported one although the fact that, generally speaking, an unsupported catalyst is more readily subject to alteration by heat indicates that there are more unsatisfied secondary valence forces, and that it might therefore be expected to be more active as an adsorbent at least so far as secondary adsorption is concerned.

It is possible that the platinised asbestos used was "poisoned" by gases such as PH_3 from the P_2O_5 which was not further purified. It was a Merck's sample. In the case of the experiments on platinum black the P_2O_5 was carefully purified by treatment with ozone. Also the platinised asbestos was heated to 370°C whereas the platinum black to only 250°C. An unsupported nickel catalyst may be spoilt by heating to 150°C, whereas a supported one may be heated to 400°C without any loss of activity, but whether similar statements would hold for platinum is not known.

The platinum black was tested for sulphur trioxide at the conclusion of the experiments. The test showed very definitely that SO_3 was present on the platinum black. It was not worth while to make quantitative determinations since in order to carry out the test the apparatus had to be opened, thus allowing oxygen from the air to come in contact with it. It was thus not possible to tell whether the sulphur trioxide was formed during the adsorption by the strongly adsorbed oxygen, or subsequently on allowing oxygen to enter.

Summary

The adsorption of sulphur dioxide by platinum black has been determined at 25°C and from O to 175 mm pressure.

The process is irreversible under the conditions of experiment.

84 Vols. of gas at N.T.P. were adsorbed per volume of platinum.

54 Vols. were retained after 8½ hours heating to 250°C.

The nature of the process has been discussed.

Acknowledgment

The author wishes to thank Prof. E. J. Hartung D.Sc. for facilities for the carrying out of this work.

Chemistry Department,
University of Melbourne,
Feb. 12, 1929.

THE CLASSIFICATION OF INDUCED REACTIONS*

BY WILDER D. BANCROFT

In 1863 Kessler[1] formulated clearly the conception of induced reactions. "Let R_α and R_β be two reducing agents (oxidizable substances), and O_α and O_β two oxidizing agents (reducible substances) of such a nature that, under certain comparable conditions, R_α reacts readily with O_α, while R_β reacts slowly or not at all with O_β. If we bring together the four substances under proper conditions and find the reaction between R_β and O_β now takes place more readily, we may consider this as induced by the reaction between R_α and O_α. So far as my experience goes, this general case of oxygen transfer can be simplified because either O_α is identical with O_β or R_α is identical with R_β. To distinguish the two cases, I will call the first case induced oxidation and the second induced reduction.

We now use the term actor[2] for the oxidizing (or reducing) agent, which reacts readily with one of the reducing (or oxidizing) agents and slowly or not at all with the other reducing (or oxidizing) agent. The substance which reacts readily with the actor is called the inductor and the substance which does not react readily with the actor is called the acceptor. The ratio of the amount of the actor reacting with the acceptor to the amount of the actor reacting with the inductor is called the induction factor.

TABLE I

Induced Oxidation

Actor	Inductor	Acceptor
Chloric acid	Ferrous salt	Indigo
Chromic acid	Ferrous salt	Potassium iodide
Chromic acid	Ferrous salt	Oxalic acid
Chromic acid	Ferrous salt	Tartaric acid
Chromic acid	Ferrous salt	Starch sugar
Chromic acid	Cuprous salt	Starch sugar
Permanganic acid	Ferrous salt	Hydrochloric acid
Permanganic acid	Ferrous salt	Tartaric acid
Permanganic acid	Arsenious acid	Tartaric acid
Permanganic acid	Antimonous salt	Tartaric acid
Oxygen	Cuprous salt	Ammonia
Oxygen	Cuprous salt	Arsenious acid
Permanganic acid	Formic acid	Ammonia

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*This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

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

[2] Schilow: Z. physik. Chem., 42, 643 (1903).

TABLE II

Induced Reduction

Actor	Inductor	Acceptor
Stannous salt	Chromic acid	Oxygen
Stannous salt	Permanganic acid	Oxygen
Stannous salt	Chlorous acid	Oxygen
Stannous salt	Hypochlorous acid	Oxygen
Stannous salt	Hydrogen peroxide	Oxygen
Stannous salt	Ozone	Oxygen
Sulphurous acid	Chromic acid	Oxygen
Sulphurous acid	Permanganic acid	Oxygen
Sulphurous acid	Iodine	Oxygen
Arsenious acid	Chromic acid	Oxygen

In Tables I and II are given the cases of induced reactions which were cited by Kessler as known in 1863. Under induced oxidations the first ten are in acid solution and the last three in alkaline solution. Under induced reductions the first eight are in acid solution and the last two in alkaline solution.

Luther and Schilow[1] have given a classification of induced reactions in which they lay great stress on the question as to which of the constituents are specific. A non-specific constituent is one for which any other oxidizing (or reducing) agent of suitable strength can be substituted, whereas this cannot be done in the case of a specific constituent. If a ferrous salt is oxidized first into an instable salt of hexavalent iron, this is specific and cannot necessarily be duplicated with some other reducing agent. If antimony oxide and tartaric acid form a complex, this is specific, because some other reducing agent would not necessarily form a complex with antimony oxide.

In Table III is given the classification of Luther and Schilow. The subscripts ox. and red. signify oxidation and reduction products, respectively.

I. Two non-specific constituents; one specific constituent

A. Actor and acceptor non-specific; inductor specific.

$\text{Actor} + \text{Fe}^{\cdot\cdot} \longrightarrow \text{Fe}^{\text{V}} + \text{Actor}_{\text{red}}.$

$\text{Fe}^{\text{V}} + \text{Acceptor} \longrightarrow \text{Fe}^{\cdot\cdot\cdot} + \text{Acceptor}_{\text{ox}}.$

B. Inductor and acceptor non-specific; actor specific.

$\text{HBrO}_3 + \text{Inductor} \longrightarrow \text{HBrO}_2 + \text{Inductor}_{\text{ox}}.$

$\text{HBrO}_2 + \text{Acceptor} \longrightarrow \text{HBr} + \text{Acceptor}_{\text{ox}}.$

C. Actor and inductor non-specific; acceptor specific.

Unknown and rather improbable case.

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[1] Z. physik. Chem., 46, 777 (1903).

II. One non-specific component: two specific components.

D. Actor non-specific; inductor and acceptor non-specific.

E. Acceptor non-specific; actor and inductor specific.

O_2(actor) + C_6H_5CHO(inductor)$\longrightarrow C_6H_5CHO_3$.
$C_6H_5CHO_3$ + Acceptor$\longrightarrow C_6H_5CO_2H$ + Acceptor$_{ox}$

F. Inductor non-specific; actor and acceptor specific.

This seems very impressive; but cases A and B are not mutually exclusive, as they should be. One can imagine a case with bromic acid as the actor and a ferrous salt as the inductor. If the first step were the formation of bromous acid and of hexavalent iron, both might then react rapidly with the acceptor. Under these circumstances, this would apparently be a special form of case E.

Miller[1] objects to Luther's classification for another reason. "In the authors' attempt to distribute the known cases of induction among their six classes, the weakness of the 'principle' on which the classification rests becomes apparent. Ferrous salts, for instance, act as inductors in fifteen reactions involving seven actors and nine acceptors—all are grouped in class A; but the eight reactions in which sulphur dioxide takes the part of inductor and in which six actors and four acceptors are involved are distributed among the remaining five classes. "This example shows how careful one must be in interpreting the phenomena of induction;" it also shows that much is left to individual opinion in the practical application of the authors' 'principle' of classification." Miller points out that Luther and Schilow were quite clear in this last point, because they say that "we consider our interpretations as in no case final."

The objection is not to the lop-sidedness of the grouping, which might actually occur, but to the arbitrariness of the assignments Miller then says: "A firmer basis for the classification may be secured by treating the problems of induction according to the methods of chemical kinetics; and comparing the rates at which the actor acts on inductor and acceptor taken each by itself, with the rates in solutions containing all three reagents together. Each case must, of course, be studied by itself; but, when the effects of all the concentrations have been ascertained, a suitable hypothesis may be founded on the results of the measurements." Miller bars out what he calls consecutive reactions. "From the theoretical point of view, the simplest cases that come under Kessler's definition are those in which the induction can be explained by the known properties of an isolable product of the reaction between actor and inductor. In order to make sure that the explanation suggested is the true one, it is only necessary to study the two reactions: actor plus inductor, and product plus acceptor, separately and compare them with the reaction which takes place in solutions containing actor, inductor, and acceptor. This has been done by Harcourt and Esson,[2] and by Bell[3] for the system H_2O_2,

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[1] J. Phys. Chem., 11, 9 (1907).

[2] J. Chem. Soc., 20, 476 (1867).

[3] J. Phys. Chem., 7, 61 (1903).

HI, $Na_2S_2O_3$; by Federlin[1] for the system $K_2S_2O_8$, HI, H_3PO_3; by Schilow[2] for the system $HBrO_3$,$HAsO_3$; and by Bowman[3] for the system $HBrO_3$, HI, $HAsO_3$. Cases like these belong demonstrably to the group of consecutive reactions, none of which were included by Kessler in his tables of examples; and it seems better to employ the term 'induced reaction' only where no such obvious explanation is available."

I do not agree with this last statement. The consecutive reactions come under the definition given by Kessler and adopted by practically everybody ever since, including Miller. As I shall show later, the case of bromic acid, chromic acid, and hydriodic acid probably comes under the head of a consecutive reaction, although classed by Miller as an induced reaction.

Miller[4] gives the following classification of induced reactions, excluding consecutive reactions:—

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

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

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

Regardless whether these classifications are sound or not, they have not proved effective. A few papers have been published in consequence of them and then the supply stopped. We are still very far from being able to say anything definite about most of the cases cited by Kessler sixty-six years ago (Tables I and II). One great trouble is that the actor very often does react with the acceptor at quite appreciable rates unless the concentrations are very low, and when the concentrations are very low the accuracy of the

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[1] Z. physik. Chem., **41**, 565 (1902).
[2] Z. physik. Chem., **42**, 641 (1903).
[3] J. Phys. Chem., **11**, 282 (1907).
[4] J. Phys. Chem., **11**, 14 (1907).

analyses is apt to be small. In the summer of 1923 I worked out a classification based on the somewhat inaccurate assumption that the reaction between the actor and the acceptor was negligible. In so far as this is not true, there is an error which must be allowed for as much as possible. The classification which I am now giving is substantially the same as that of six years ago. It is based on determinations of the induction factor and not on reaction velocity measurements. While I should have liked to have tested it further, that means holding up theses longer than is right.

Let A = actor, B = inductor, and C = acceptor. If A is an oxidizing agent, the induction factor, I.F., equals C_{ox}/B_{ox}. We recognize the following cases.

1. B may catalyze the reaction between A and C, besides reacting with A. The induction factor will increase indefinitely[1] with relative increase of C, if one adds A to a mixture of B and C. The induction factor will approach a low value, perhaps zero, if one adds B to a mixture of A and C so slowly that B is used up practically instantaneously. Clark[2] found that chromic acid catalyzes the reaction between bromic acid and hydriodic acid without itself being reduced. Since chromic acid reacts readily with hydriodic acid when bromic acid is not there, this statement of facts, surprising though it is, seems to justify putting the system A = $HBrO_3$, B = H_2CrO_4, and C = HI under case 1. On the other hand, we know that bromic acid will oxidize a chromic salt to chromic acid under suitable conditions and it therefore seems probable that this is really a consecutive reaction, coming under 3a, with A = $HBrO_3$, B = CrO_3, and C = HI. The bromic acid would oxidize the chromic oxide or salt to chromic acid, and the chromic acid would oxidize the hydriodic acid to iodine.

2. C may react with a reduction (or oxidation) product of A. Slow addition of B to a mixture of A and C will give a definite induction factor. With B in excess, addition of A to a mixture of B and C will give an induction factor approaching zero. With C in excess, slow addition of A to a mixture of B and C will give an induction factor approaching the definite value obtained on adding B to a mixture of A and C. Schilow[3] studied the system A = $HBrO_3$, B = H_2SO_3, and C = As_2O_3. The conditions can be so arranged that one oxygen from the bromic acid will oxidize the sulphurous acid, while the two oxygens from the resulting bromous acid oxidize the arsenious acid. The induction factor is therefore two.

3a. C may react rapidly with a stable addition product of A and B or with a stable oxidation (or reduction) product of B and not directly with A or with one of its reduction (or oxidation) products at any appreciable rate. So long as C is present, B will appear to be unchanged because it is at once regenerated by reaction with C. If there is some A left when C is decomposed completely, we shall get the oxidation (or reduction) product of B. This is what has been called a consecutive reaction.

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[1] Cf. Luther and Schilow: Z. physik. Chem., **46**, 783 (1903).

[2] J. Phys. Chem., **11**, 353 (1907).

[3] Z. physik. Chem., **42**, 541 (1903).

Miss Bush[1] has studied the system $A = O_2$, $B = HI$, and $C = H_2SO_3$. Atmospheric oxygen reacts much more rapidly with hydriodic acid than it does with sulphurous acid, while iodine reacts rapidly with sulphurous acid. Consequently it is easy to arrange it so that air oxidizes hydriodic acid and the iodine oxidizes the sulphurous acid. In this as in other consecutive reactions, the induction factor is one, because each equivalent of oxygen is passed on. This is a clear-cut case of a homogeneous catalysis with intermediate formation of a definite chemical compound. In so far as the hydrogen ion of the hydriodic acid may catalyze the reaction between oxygen and sulphurous acid, this might be considered as coming under Case I.

If we wish to consider sulphurous acid as actor and oxygen as acceptor, we may do so, because these two substances are non-specific in the sense that Luther and Schilow used it. The oxidation product of the inductor now becomes the inductor, and we write the system $A = H_2SO_3$, $B = I_2$, and $C = O_2$.

Milas[2] has studied the system A = furfural, $B = V_2O_5$, and C = chlorate. Furfural reduces yellow V_2O_5 to blue V_2O_4, and then to green V_2O_3, while chlorate reverses these changes. One could also consider this as the system A = chlorate, $B = V_2O_3$, and C = furfural.

Hofmann[3] finds that air will oxidize osmium dioxide to osmium tetroxide, and that osmium tetroxide will oxidize alcohol to acetaldehyde. We may, therefore, consider this as an induced reaction with $A = O_2$, $B = OsO_2$, and C = alcohol. Bowman[4] has studied the system $A = HBrO_3$, $B = HI$, and $C = As_2O_3$. There is no evidence that there is any appreciable reaction between $HBrO_3$ and As_2O_3, the whole oxidation of the arsenious acid being due to the iodine. This apparently differs from the case studied by Schilow of $A = HBrO_3$, $B = H_2SO_3$, and $C = As_2O_3$ in that the sulphuric acid formed by the oxidation of sulphurous acid does not oxidize arsenious acid as iodine does.

Federlin[5] finds that the reactions between persulphate and hydriodic acid, and between iodine and phosphorous acid, H_3PO_3, are moderately fast, while there is no reaction between persulphate and the phosphorous acid. Consequently we are dealing with a consecutive reaction in the system $A = H_2S_2O_8$, $B = HI$, and $C = H_3PO_3$.

3b. C may react rapidly with an instable addition product of A and B or with an instable oxidation (or reduction) product of B and not directly with A or with one of its reduction (or oxidation) products at any appreciable rate. Thus we might have $A + Fe^{II} \longrightarrow A_{red.} + Fe,^{VI}$ and Fe^{VI} reacts with C. If B is added slowly to a mixture of A and C, the limiting induction factor should be obtained, because there is less danger in this case of hexavalent iron reacting with bivalent iron if the concentration of bivalent iron

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[1] J. Phys. Chem., 33, 613 (1929).

[2] J. Am. Chem. Soc., 49, 2005 (1927).

[3] Ber., 45, 329 (1912); 46, 1657 (1913).

[4] J. Phys. Chem., 11, 292 (1907).

[5] Z. 41, 565 (1902.

is kept as near zero as possible. If B is added to A alone, there will be an evolution of oxygen, which will be proportional to the amount of B added. At first sight it seems as though one could determine the composition of the instable compound in this way. If nothing else happened, one could do so; but there is often a catalytic evolution of oxygen which will complicate matters unless one can correct for it.

B is specific; but A may be any suitable oxidizing (or reducing) agent. If there are two or more instable forms of B, such as Fe^{IV} and Fe^{VI} for instance, the one that is obtained will depend on the strength of the oxidizing (or reducing) agent. Manchot[1] believed that he had Fe_2O_5 as instable intermediate compound with hydrogen peroxide permanganate and Fe_2O_4 with oxygen. Hale[2] has confirmed the Fe_2O_4; but he finds that the other compound is FeO_3 and not Fe_2O_5. With a strong oxidizing agent, we get the higher instable oxide:

$A = H_2O_2$, $B = Fe^{II} \longrightarrow Fe^{IV}$, and $C = KI$.
$A = KMnO_4$, $B = Fe^{II} \longrightarrow Fe^{VI}$, and C = sodium arsenite.

With a weaker oxidizing agent, we get the lower instable oxide:

$A = O_2$, $B = Fe^{II} \longrightarrow Fe^{IV}$, and C = sodium arsenite

These experiments make it practically certain that the instable oxide on passive iron is FeO_3; but there are some more experiments to be done before that problem can be said to be solved definitely.

The possibility of an instable addition product cannot be denied; but it is not easy to see at present just how one can differentiate this in a general way from the case of an instable oxidation (or reduction) product of B. To take a definite case, let us consider $A = H_2O_2$ and $B = Fe^{II}$. So far as I can see now, the intermediate compound might be written $Fe.^{II}{}_3H_2O_2$ or Fe^{V}.

If the activation of oxygen by benzaldehyde or triethylphosphine[3] is due to the intermediate formation of a peroxide as Engler and Weissberg assume, we are dealing with an instable addition product if we cannot isolate it and a stable one if we can. In the first case the system will come under 3b and in the second under 3a.

The dividing line between 3a and 3b is somewhat arbitrary, because the reaction product of A and B might be stable under one set of conditions and instable under another set.

Under certain circumstances, it may be practically impossible to distinguish by general methods between cases 3b and 4. If we postulate that $A = O_2$, $B = Zn$. and $C = H_2O$, and that the reactions are $O_2 + Zn = ZnO_2$ and $ZnO_2 + H_2O = ZnO + H_2O_2$, this system comes under case 3b if the ZnO_2 is instable under the conditions of the experiment. Addition of zinc slowly to a solution of oxygen in water will give a definite induction factor

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[1] Ber., 34, 2477 (1901).
[2] Cornell University Thesis (1928).
[3] Jorissen: Z. physik. Chem., 22, 34 (1897).

of one; but this is complicated by the instability of hydrogen peroxide. If zinc peroxide is instable, we shall get evolution of oxygen on addition of oxygen to zinc; but it is hard to distinguish this from a direct reaction to zinc oxide with no evolution of oxygen. The conditions under which we may class this system under case 4 will be taken up when discussing case 4.

There is another interesting possibility under 3b. We know that hydrogen peroxide reacts with certain peroxides in such a way that each substance loses oxygen. It is immaterial for the moment whether the first step is the formation of an instable addition compound of the two substances or whether one oxidizes the other to a higher oxidation product. It is conceivable that the oxygen would oxidize some compound which neither could oxidize alone. We seem to have a case of this sort with chlorate and osmium tetroxide.[1] If one adds 0.01% OsO_4 to a saturated potassium chlorate solution, the mixture oxidizes manganous acetate or soot and attacks iron, lead, copper, etc. The details are not sufficient to enable one to be absolutely certain; but it looks like a special form of induced reaction. The solution oxidizes carbon monoxide when adsorbed on palladium but not hydrogen.

4. B and C form a complex or a reaction product which reacts with A. What will happen will depend on the rate of formation and the degree of dissociation of the complex, and on the relative rates of reaction of the complex and of B with A. If we add A to a mixture of B and containing so much of C that there will be no free B, we shall get a definite induction factor provided the rate of reaction of A with C is negligible. Addition of B to a mixture of A and C will give values of the induction factor varying between zero and the limiting value, depending on the relative rates. A case of this sort is the system[2] A = AgBr or Ag_2O, B = hydroquinone, C = sodium sulphite. Silver bromide and silver oxide oxidize hydroquinone but not sodium sulphite. They oxidize sodium sulphite in presence of hydroquinone.

Instead of B and C forming a complex as happens with hydroquinone and sodium sulphite, they may react to give a product which reacts with A. If we take the system A = O_2, B = Zn, and C = H_2O, previously discussed under 3b, and postulate the reactions $Zn + H_2O = ZnO + 2H$ and $2H + O_2, = H_2O$ this system belongs under case 4. Addition of oxygen to a mixture of zinc and water should give a definite induction factor if we can ignore the reaction between oxygen and zinc and between oxygen and water. The second reaction is negligible and the first can be made negligible by making the system into a cell and introducing the oxygen at the cathode. With this arrangement the system belongs unquestionably under case 4. Since we keep the oxygen from coming in contact with the zinc, we have prevented the possibility of zinc peroxide being formed and consequently the experiment proves nothing in regard to the general behavior of the system.

There seems to be a difference between cases 3 and 4 when we add B slowly to a mixture of A and C, because under case 3b we should get a definite

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[1] Hofmann: Ber., 45, 1662, 3329 (1912); 46, 1657 (1913).

[2] Gordon: J. Phys. Chem., 17, 47 (1913).

induction factor, while under case 4 the induction factor may vary between the limit and zero depending on the relative rates of reaction. This does not prevent the relative rates being such that in the system O_2, Zn, and H_2O, the induction factor may and does have a definite value. With sodium substituted for zinc, it would probably be difficult to prevent an evolution of hydrogen and a consequent dropping of the induction factor towards zero.

The general method will therefore not enable us to decide whether we do or do not have a primary formation of zinc peroxide when zinc, liquid water, and oxygen are in contact. I decide it for myself on other grounds. The corrosion of zinc in presence of liquid water is unquestionably an electrolytic phenomenon and consequently cannot involve the formation of zinc peroxide. On the other hand sodium burns in the air to sodium peroxide and zinc may do likewise. It seems to me quite possible that there may be a primary formation of zinc peroxide in the system O_2, Zn, and water vapor at temperatures above those at which zinc is wetted by the water vapor. This is the view put forward and for the same reasons by Haber[1] nearly thirty years ago. Since benzaldehyde cannot react with water to give hydrogen, it probably reacts with oxygen to form a peroxide.

5. Nos. 1–4 may occur simultaneously in any grouping. We might have $2HBrO_3 + FeO \longrightarrow 2HBrO_2 + FeO_3$, and both of these might react with C. Case 5 will usually be recognized by positive tests in at least two of the preceding cases. Each problem will then have to be considered on its own merits.

The general results of this paper are as follows:

1. A classification of induced reactions has been given which is based on the induction factor as determined when the reaction has reached an end. This eliminates the difficulty in interpreting reaction velocity experiments; but is liable to serious error if the actor reacts at any appreciable rate with the acceptor.

2. All the induced reactions studied so far can be arranged in three groups or in combinations of these groups. The acceptor may react with a lower stage of the actor. The acceptor may react with a reaction product of the inductor. The actor may react with a reaction product of the inductor and acceptor.

3. Consecutive reactions should be classed under induced reactions. They are reactions in which the acceptor reacts with a stable oxidation or reduction product of the inductor.

4. When a ferrous salt acts as an inductor, the instable oxidation product may be either Fe^{IV} or Fe^{VI}, depending on the strength of the actor *us* an oxidizing agent.

5. The activation of oxygen by benzaldehyde is probably the result of a peroxide formation. The activation of oxygen by zinc in the presence of liquid water is not due to the intermediate formation of zinc peroxide.

Cornell University.

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[1] Z. physik. Chem., **34**, 513; **35**, 81.

THE BOILING-POINT ELEVATION OF ACETONE SOLUTIONS AS RELATED TO THE INTERIONIC ATTRACTION THEORY*

BY A. L. ROBINSON

The 'Interionic Attraction' theory of Debye and Hückel[1] has had considerable success in explaining many anomalous properties of aqueous solutions of strong electrolytes. The behavior of dilute non-aqueous solutions of strong electrolytes has also been interpreted by the same theory with a fair degree of success in a number of instances.[2] The theory has also been applied to solutions of strong electrolytes in mixed solvents.[3]

The original purpose of these ebullioscopic measurements was to further test the validity of applying the Debye-Hückel theory to dilute acetone solutions of strong electrolytes.[4] The deviation of the observed freezing point or boiling point changes from the values calculated from the classical theory, assuming complete ionization in the calculation, is given by equation (41) of Debye and Hückel

$$1 - f_o = \frac{\Delta_c - \Delta}{\Delta_c} = w \frac{e^2}{6DkT}\sqrt{\frac{4\pi e^2}{DkT} nv}\, \frac{\Sigma v_i z_i^2 \sigma}{\Sigma v_i z_i^2}$$

where f_o is the osmotic coefficient, Δ_c and Δ are the calculated and observed values of the boiling point change, w is a valence factor equal to $\left(\frac{\Sigma v_i z_i^2}{\Sigma v_i}\right)^{3/2}$, e is the elementary electrical charge, D is the dielectric constant, k and T are the gas constant and the absolute temperature, n is the number of moles of dissolved salt per 1000 grams of solvent and v is the number of ions furnished by one molecule of the salt, v_i and z_i are the number and valence of ions of the ith kind furnished by a single molecule of solute, and σ is a function of 'a', the mean apparent ionic diameter, and the total concentration. In ordinary 'dilute' solutions σ will be less than unity (it becomes equal to unity in the ideal dilute region, where the ions may be treated as point charges). The above relations for acetone at the boiling point becomes

$$1 - f_o = 2.46w\sqrt{nv\sigma}$$

using 56.1°C as the boiling temperature and 16.5 as the dielectric constant, this latter value being extrapolated from the measurements of Drude.

By plotting (1-f_o) against $\sqrt{nv}$ a curve should be obtained which goes into the origin with a slope of 2.46w; furthermore, from the shape of the curve it

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* Contribution from the Department of Chemistry, University of Pittsburgh.

[1] Debye and Hückel: Physik. Z., **24**, 185 (1923).

[2] Noyes and Baxter: J. Am. Chem. Soc., 47, 2122 (1925); Webb: **48**, 2263 (1926); Schreiner and Frivold: Z. physik. Chem., **124**, 1 (1926); Frivold: J. Phys. Chem., **30**, 1202 (1926).

[3] McAulay: J. Phys. Chem., **30**, 1202 (1926).

[4] Robinson: J. Phys. Chem., **32**, 1089 (1928).

[5] Drude: Z. physik. Chem., **23**, 267 (1897).

should be possible to determine σ for each solute, and, by using the values given for this function in Table I of the Debye-Hückel article, values for 'a', the mean ionic diameter, can be calculated.

In addition to the test outlined above it was thought that some light might be thrown on the question of hydration and apparent ion size by using hydrated as well as anhydrous salts.

Experimental

The measurements were made with boiling-point apparatus described by Menzies and Wright[1] and a differential thermometer constructed by Menzies.[2] At the boiling point of acetone this thermometer allows the measurement of temperature differences with an accuracy of 0.001°C.

The acetone was first dehydrated over $CaCl_2$, distilled, and then further dehydrated over sodium amalgam, or refluxed for some time with anhydrous K_2CO_3. When distilled again, the fraction boiling between 56.08° and 56.12°C was collected for use. The temperature was read with a thermometer recently checked by the Bureau of Standards and was corrected to 760 mm.

The salts were C.P. preparations and were recrystallized several times and dried to the desired composition, as determined by analysis. The $La(NO_3)_3$ was a preparation kindly furnished by Professor James; it was allowed to stand for a long time in a vacuum desiccator over P_2O_5, and then heated carefully to constant weight. Frivold[3] has shown that the anhydrous salt prepared in this way contains no basic nitrate.

Results

In Table I *n* is the concentration of dissolved salt in mols per 1000 grams of solvent, $\sqrt{nv}$ is the square root of the ionic concentration, Δ_o is the calculated boiling point rise ($\Delta_o = 1.72nv$), Δ is the observed boiling point rise, and $1-f_o$ is the deviation of the osmotic coefficient from unity.

TABLE I
NaI
First Series

n	$\sqrt{nv}$	Δ_o	Δ	$1-f_o$
0.00389	0.088	0.0134	0.0130	0.150
0.00680	0.117	0.0234	0.0183	0.216
0.02627	0.219	0.0904	0.0678	0.250
0.05805	0.341	0.1995	0.1390	0.303
0.0916	0.428	0.315	0.2187	0.305
0.1318	0.514	0.453	0.2838	0.373
0.1746	0.591	0.601	0.355	0.405
0.2206	0.665	0.754	0.443	0.412
0.3440	0.831	1.182	0.661	0.441

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[1] Menzies and Wright: J. Am. Chem. Soc., 43, 2314 (1921).

[2] Menzies: J. Am. Chem. Soc., 43, 2309 (1921).

[3] Frivold: J. Phys. Chem., 30, 1155, 1926.

TABLE I (Continued)

n	$\sqrt{nv}$	Δ_0	Δ	$1\text{-}f_0$
Second Series				
0.00856	0.131	0.0295	0.0243	0.176
0.0174	0.187	0.0599	0.0468	0.219
0.0351	0.265	0.1208	0.0880	0.272
0.1268	0.504	0.436	0.290	0.334
0.1798	0.600	0.618	0.386	0.375
Third Series				
0.00803	0.127	0.0276	0.0220	0.195
0.0425	0.292	0.1463	0.1072	0.267
0.0725	0.381	0.2495	0.1760	0.293
0.1550	0.549	0.534	0.331	0.379
0.2561	0.716	0.908	0.514	0.433
$NaI.2H_2O$				
First Series				
0.00243	0.070	0.0084	0.0076	0.095
0.0292	0.242	0.1004	0.0769	0.235
0.0714	0.391	0.2456	0.1786	0.282
0.1104	0.470	0.380	0.254	0.302
Second Series				
0.0153	0.175	0.0525	0.0430	0.181
0.0230	0.215	0.0790	0.0564	0.286
0.1089	0.468	0.375	0.254	0.324
0.1398	0.529	0.481	0.300	0.376
$CoCl_2$				
First Series				
0.00136	0.064	0.0074	0.0049	0.338
0.00783	0.153	0.0404	0.0159	0.606
0.0235	0.265	0.1210	0.0366	0.696
0.0558	0.409	0.288	0.072	0.750
0.1956	0.766	1.009	0.218	0.785
0.2830	0.923	1.460	0.290	0.803
Second Series				
0.00386	0.108	0.0199	0.0089	0.553
0.0304	0.302	0.1570	0.0538	0.657
0.0931	0.529	0.480	0.122	0.745
0.1620	0.698	0.836	0.177	0.787
0.2431	0.855	1.256	0.217	0.828

TABLE I (Continued)

n	$\sqrt{nv}$	Δ_0	Δ	$1-f_0$
		Third Series		
0.00176	0.073	0.0091	0.0055	0.396
0.00718	0.147	0.0371	0.0175	0.529
0.0702	0.460	0.352	0.095	0.725
0.2582	0.875	1.332	0.278	0.792
		$CoCl_2.6H_2O$ First Series		
0.00292	0.094	0.0150	0.0081	0.470
0.00879	0.163	0.0454	0.0191	0.579
0.0182	0.234	0.0938	0.0319	0.659
0.0398	0.346	0.205	0.050	0.760
0.0754	0.477	0.389	0.097	0.746
0.1343	0.660	0.683	0.137	0.800
		$La(NO_3)_3$ First Series		
0.000856	0.059	0.0059	0.0038	0.350
0.00243	0.099	0.0167	0.0089	0.467
0.0140	0.237	0.0964	0.0255	0.735
0.0262	0.324	0.180	0.046	0.745
		Second Series		
0.00168	0.082	0.0115	0.0064	0.440
0.00424	0.130	0.0292	0.0116	0.603
0.0121	0.220	0.0833	0.0304	0.635
0.0424	0.413	0.292	0.068	0.767
		$La(NO_3)_3.6H_2O$ First Series		
0.00164	0.081	0.0113	0.0064	0.390
0.00391	0.125	0.0269	0.0128	0.525
0.00944	0.189	0.0644	0.0253	0.607
0.0185	0.272	0.1272	0.0365	0.713
0.0371	0.385	0.255	0.055	0.787

Discussion of Results

In Figs. 1, 2, and 3 are plotted the values of $(1-f_0)$ against $\sqrt{nv}$ for NaI, $CoCl_2$, and $La(NO_3)_3$ respectively (the solid circles represent the data for the hydrated salts). In each Figure the straight line going into the origin is drawn for the theoretical relation $1-f_0 = w(2.46)\sqrt{nv}$ (w has the values of 1, 2.83, and 5.2 for the salts in the order listed). Although too much weight should not be given to the observations at the lowest concentrations it seems

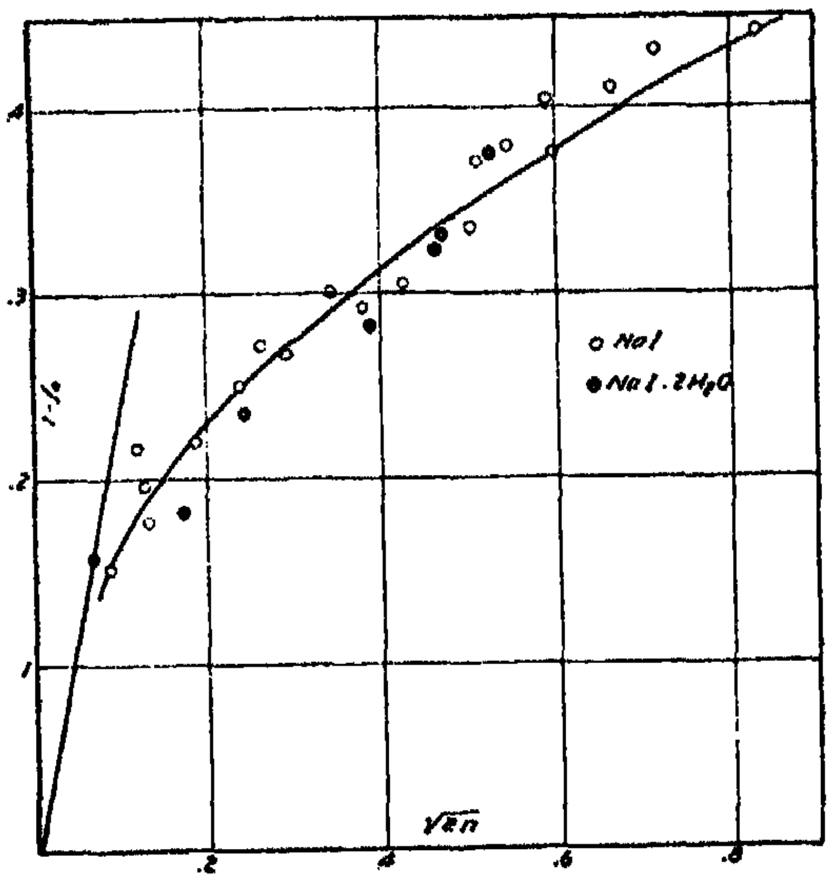

FIG. 1

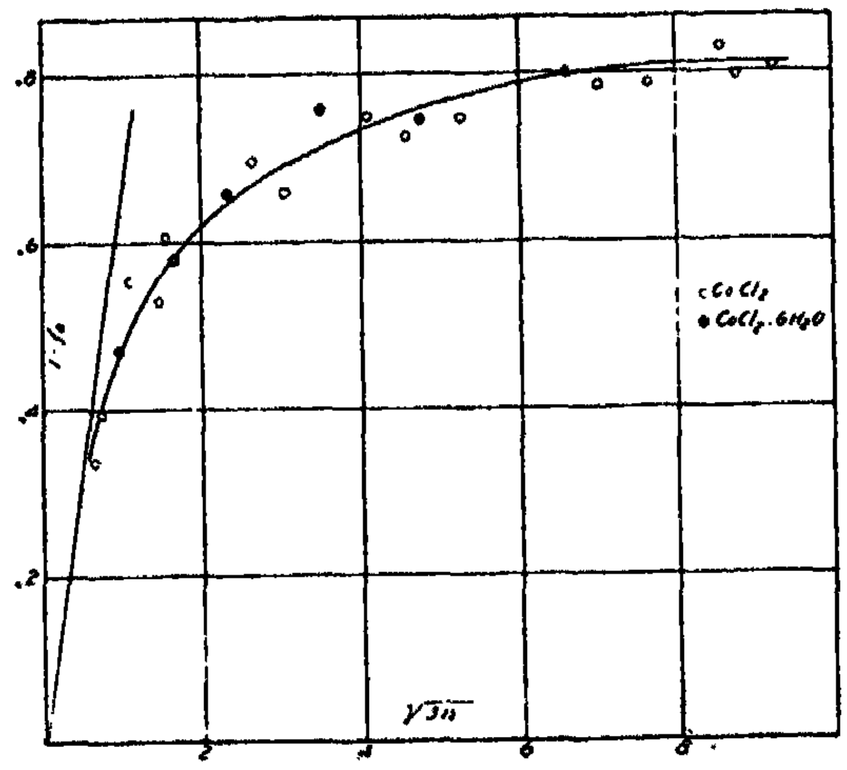

FIG. 2

that the experimental curves are straightening out preparatory to going into the origin at an angle very close to the one indicated by the above relation. In particular the validity of the valence factor w seems to be confirmed. By the method outlined by Debye and Hückel,[1] using their Table I, values for 'a', the mean ionic diameter, have been calculated which closely fit the experimental curves. They are as follows—

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[1] Debye and Hückel: loc. cit.

Salt	$a.10^8$ cm.
NaI	2.03
$CoCl_2$	2.95
$La(NO_3)_3$	4.42

These values are certainly of the correct order of magnitude for the ionic diameters. No particular significance should be attached to their exact values, inasmuch as theory of Debye and Hückel, in introducing the parameter 'a', makes use of certain arbitrary assumptions in connection with the shape of ions. Moreover, LaMer[1] has shown that values of 'a' calculated by fitting equation (41) to experimental data are only first approximations, and in general the more accurate values are somewhat higher.

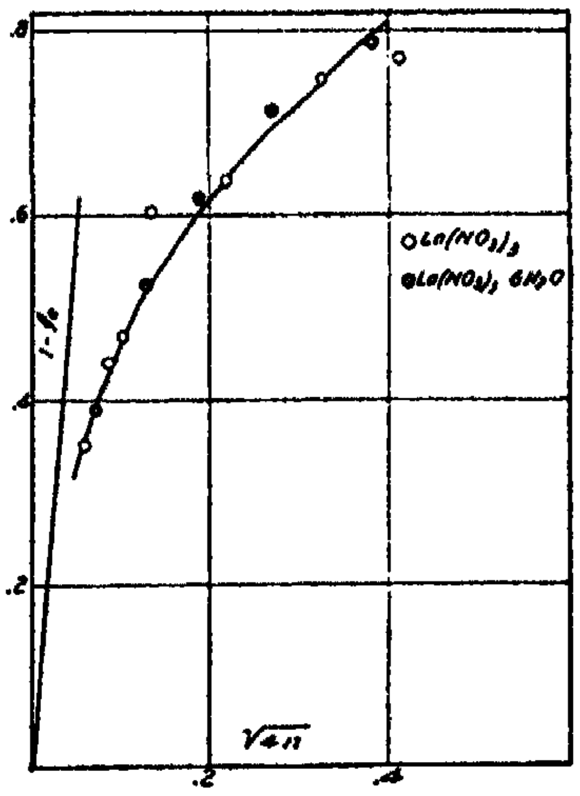

FIG. 3

It is observed that the same curve, in the case of each salt, fits the data both for the unhydrated and hydrated salt. Debye[2] has suggested a picture of the distribution of water and non-electrolyte in the immediate vicinity of an ion. The more easily polarisable water molecules seek the strong fields close to the ions, so that in a mixed solvent of the type mentioned the concentration of water rises rapidly as the ion is approached, and near the surface of the ion only water molecules are present. As a result of this distribution the dielectric constant of the medium surrounding the ions is not the same as the rest of the solvent, but varies with the distance from the ion, the two becoming identical at large distances. The attraction of the solvent molecules by the ions gives rise to a pressure which causes a compression of the solvent in the vicinity of the ion. According to calculations of Webb[3] the values of this pressure become very large as the surface of the ion is approached. They are of the order 10^3 megadynes/cm.^{2} at 3 Å from the center of the ion and 3×10^4 megadynes/cm.^{2} at 1.55 Å, for water. The effective charge of the solvent molecule dipole largely determines these forces.

It seems reasonable to suppose that the ions, as well as the solvent, suffer a contraction of volume as a result of this electrical pressure and this effect, whatever its magnitude, should be greater in solvents of high dipole moment, such as water, than in non-aqueous solvents of lower dielectric constant.

The apparent size of ions in solutions will also be determined by the firmness with which the solvent molecules are bound to the ions. The opinion

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[1] LaMer: Trans. Am. Electrochem. Soc., 51, 507 (1927).

[2] McAulay: J. Phys. Chem., 30, 1202 (1926).

[3] Webb: Trans. Am. Electrochem. Soc., 51, 690 (1927).

generally held at present is that the hydrogen ion alone is definitely chemically hydrated as the H_3O^+ ion; other ions are surrounded by oriented water molecules held less firmly, depending on the size and charge distribution of the ions. These oriented molecules may be carried by the ion as it moves; the distribution of water and other molecules around an ion remains on the average constant, although this distribution may be continuously changing due to thermal agitation and collisions.

The same mean ionic diameters for hydrated and anhydrous salts will account for the observed data, using the same dielectric constant for both types of solutions. Using a somewhat higher value of this constant for the solutions of the hydrated salts (an integration should be performed from $r = a$ to $r = \infty$) lower values of 'a' would be obtained than the values given above. It seems then that these ions do not form definite hydrates, as far as any conclusion can be drawn from the use of the Debye and Hückel theory.

Summary

Boiling point measurements have been made of acetone solutions of NaI, $CoCl_2$, and $La(NO_3)_3$ between the concentration range 0.001-0.3M. Both anhydrous and hydrated salts were used. For the three valence types of salts the results are in excellent accord with the interionic attraction theory of Debye and Hückel.

The results obtained using hydrated salts have been interpreted as indicating the non-existence of definite ionic hydrates.

Pittsburgh, Pennsylvania.

ON THE PRIMARY PROCESS OF LIGHT ABSORPTION AND ACTIVATION IN PHOTOCHEMICAL REACTIONS

BY KALI PADA BASU

All photochemical reactions must, according to the present state of our knowledge, be governed by two fundamental laws. The first is the Grotthuss-Draper absorption law. The second is Einstein's law which states that the process of absorption of radiation is a quantised process, only one excited system (molecule or atom) being produced for each quantum absorbed. The subsequent course of reaction depends, as is now held, on the properties of the excited system which may give the same number of resultant molecules as excited ones or more.

As a result of numerous experiments performed most carefully by various investigators it has been definitely established that almost invariably a large number of resultant molecules are formed by the absorption of a single quantum of radiation. This is explained by a chain mechanism which either (1) postulates the production of a free atom or group which enters into the reaction and is regenerated as a reaction product or (2) assumes a succession of radiation-less transfers of energy from energy-rich activated molecule of one of the products to activate a reactant molecule by collision.

It is the purpose of this paper to show that a single quantum of radiation need not produce only one activated molecule but can, under suitable conditions, produce more than one, say four or five activated molecules.

That part of an incident quantum of radiation can be absorbed by a medium and the remaining part can appear as a scattered quantum of modified frequency was first hinted by Smekal.[1] Kramers and Heisenberg[2] and also Schrodinger[3] inclined to this view. But no experimental evidence for this was forthcoming. Recently the brilliant investigations of Prof. Raman and his coworkers have furnished definite proof[4] of the possibility of such a process. Prof. Raman has shown definitely that a part of a quantum of incident radiation can be absorbed by a molecule of a medium and the remainder scattered as a quantum of modified frequency, and the shift of frequency has been shown to agree with certain characteristic infra-red frequencies of the molecule.

We can now extend this idea to the primary process of absorption and activation in photochemical reactions. A molecule of the photoactive component in a photochemical reaction absorbs a part of the quantum of the incident photochemically effective radiation, is thereby raised to a higher

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[1] Naturwiss; **11**, 873 (1923).

[2] Z. Physik, **31**, 681 (1925).

[3] "Abhandlungen zur Wellenmechanik," 112 (1927).

[4] Raman: Ind. J. Physics, **2**, 387; Raman and Krishnan: 399 (1928); Proc. Roy. Soc., **122A**, 23 (1929).

level of energy, and possesses sufficient energy (as is demanded by the energy of activation of the process) to initiate the chemical reaction. The remainder of the quantum is scattered by the molecule a part of which again is absorbed by another molecule and a part scattered. This process will go on till there is as much absorption of incident radiation as is demanded by the observed extinction coefficient of the photoactive component. The process can thus well extend over several molecules and in each case, though only a part of the quantum is absorbed by a molecule in agreement with a characteristic infra-red frequency, the molecules will have sufficient energy to react, since this energy will be greater, as will be presently shown, than the energy of activation of the process. We shall now discuss the question of energy of activation in photochemical processes.

It is well known that a reaction that proceeds under stimulus of light energy at the ordinary temperature can go on in darkness at an elevated temperature giving the identical products. The temperature coefficient of the dark reaction at once gives us, through the Arrhenius equation, the energy which an active molecule should possess in excess of the average energy of molecules. The temperature coefficient of the dark reactions generally varies from 2 to 3. Application of the Arrhenius equation for a temperature coefficient of 2.5, leads to the following value for the heat of activation.

$$2.3 \times \log_{10} 2.5 = \frac{Q}{R}\left(\frac{1}{273 + 30} - \frac{1}{273 + 40}\right)$$

where Q is the heat of activation. This gives the value 17,360 calories for Q. This corresponds to energy per gm. mol corresponding to absorption of radiation in the infra-red, the extreme red region (7600Å) corresponding to about 37,000 calories per gm. mol. Violet light (4000Å) corresponds to an energy of about 70,000 calories per gm mol and we can thus conceive of a quantum of incident radiation bringing four or five molecules into a sufficiently active state to be able to initiate reaction.

While the temperature coefficient of the corresponding dark reaction gives a value of about 17,000 calories for the heat of activation it is probable that, due to absorption of light in photochemical reactions, the energy of activation itself for the reaction is lowered. It is well known that, according to modern views about the mechanism of action of a catalyst in a catalysed reaction, the function of the catalyst is to lower, the heat of activation by distorting the atom or molecule.[1]

It has recently been observed that the temperature coefficient for the enzymatic inversion of cane sugar[1] is lower than the temperature coefficient without the enzyme. Hinshelwood gives the following examples (p. 188) of the lowering of heat of activation in a catalyzed reaction.

The catalysed reactions have thus heats of activation about half as great only as the homogeneous changes. A catalyst does this by distorting the

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[1] Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," p. 184; Burk: J. Phys. Chem., 32, 1601 (1928).

molecule or atom. Now there is some similarity between a photochemical reaction and a catalysed reaction. Absorption of radiation undoubtedly distorts the absorbing atom or molecule, in that an electron is removed to a higher quantum orbit. A photochemical reaction should thus have a lower energy of activation than the corresponding dark reaction. The lowering of the energy of activation should be greater the greater the distortion produced and we can thus explain the observed diminution in the temperature coefficient of the photochemical reactions with increase in frequency.

Reaction Thermal decomposition of:—	Total activation required for homogeneous change.	Total activation required for catalyzed change
Hydrogen iodide	44,000 calories	25,000 (gold)
Nitrous oxide	58,500	29,000 (gold) 32,500 (platinum)
Ammonia	probably >80,000	39,000 (tungsten)

If the heats of activation of a photochemical reaction should be considerably lower than 17,000 calories, it is thus evident that on the basis of the conceptions outlined above, a quantum of visible or ultraviolet radiation can activate 8-10 molecules. While chain reactions might play their part in photochemical reactions this factor to which we draw attention should receive some consideration.

Effect of Wave-length on Quantum Efficiency. According to Einstein's law the quantum efficiency should be independent of wave-length. This is far from being the case in actual experiments. Reviewing the field Prof. Allmand,[1] in his introductory address to the Faraday Society discussion, says, "No case is known in which γ (i.e. quantum efficiency) increases with λ . . . In *the majority of cases, γ increases as λ decreases,* corresponding to the universal tendency towards increased photosensitivity at shorter wave-lengths. *In respect therefore of the effect of wave-length, the Einstein law holds badly in practice.*"

We shall give only a few examples. Thus in the decomposition of H_2O_2 studied by Henri and Wurmser (1913), the quantum efficiency is 4.5 at 280 $\mu\mu$, 6 at 208$\mu\mu$ and 130 at 230$\mu\mu$. In the decomposition of potassium cobalti-oxalate investigated by Vranek[2] the quantum efficiency is 0.6 at 436$\mu\mu$, 0.9 at 405$\mu\mu$ and 1.5 at 366$\mu\mu$. In the photochlorination of cinnamic acid recently investigated by the present author the quantum efficiency is 2 at 436$\mu\mu$, 4 at 404$\mu\mu$ and 7 at 366$\mu\mu$. Numerous other examples are to be found in the introductory address of Prof. Allmand.

The mechanism of absorption and activations that we have outlined above very easily explains the observed increase in quantum efficiency with increase in frequency. Rayleigh's fourth-power law postulates that scattering is proportional to λ^{-4}. Scattering and the number of molecules acti-

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[1] Trans. Faraday Soc., 21, 447 (1925).

[2] Z. Elektrochemie (1917).

vated should thus increase with increase in frequency. It is probable that if the reaction vessels in photochemical reactions had their sides silvered so as to present any escape of radiation by scattering, even those few reactions which show an identical quantum efficiency at different wave-lengths would show an increase in efficiency with increases in frequency.

Such a conception as has been outlined above enables us to explain how molecules of many substances show an absorption of energy many times the energy of dissociation and still show no sign of dissociation. Thus iodine molecules absorb light of wave-length 1849 Å—a quantum of which corresponds to an amount of energy five times the energy necessary to dissociate a molecule of iodine, but are not dissociated.

Summary

The abnormal yield per quantum of radiation absorbed in photochemical reactions has been shown to be due partly to the fact that one quantum of incident radiation can activate more than one molecule of the absorbing substance. The increase of photochemical efficiency with increase in frequency of incident radiation which cannot be explained on the basis of Einstein's law, has also been explained.

My best thanks are due to Prof. J. C. Ghosh and Prof. S. N. Bose for their kind interest and many valuable suggestions.

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NEW VIEWS ON AUTO-OXIDATIONS[*]

BY NICHOLAS A. MILAS[1]

Our constantly increasing knowledge of auto-oxidation reactions since the inception of the Engler-Bach[2] theory, has brought forth new but conflicting and at times irreconcilable interpretations of the mechanism of such reactions. Although the Engler-Bach theory gave a reasonable explanation of auto-oxidations, Wieland[3] has challenged its validity by presenting new experimental evidence to prove that oxidations with atmospheric oxygen are not preceded by the addition of molecular oxygen to "auto-oxidants," as the Engler-Bach theory originally assumed, but by the removal of hydrogen atoms which are subsequently absorbed by the oxygen molecules to form hydrogen peroxide as the primary product. In other words, Wieland's theory assumes an initial "dehydrogenation" of the auto-oxidant followed by an activation of the hydrogen atoms, whereas the Engler-Bach theory assumes an initial addition of oxygen molecules to the auto-oxidant followed by the formation of "active" oxygen. To explain the numerous auto-oxidations in which the auto-oxidant is deficient in hydrogen, Wieland made the assumption that water should add on to the auto-oxidant before it can be dehydrogenated.

That Wieland's contention does not hold with "true" auto-oxidations, is borne out by much chemical and biological evidence. It will be beyond the scope of this paper to attempt to give a complete list of such oxidations; only a few representative examples will suffice to show the inadequacy of Wieland's view. Lothar Meyer[4] was the first to observe that rigidly-dried mixtures of carbon monoxide and oxygen could be made to combine non-explosively, while the more recent and more reliable experiments of Bone and his students[5] proved beyond any reasonable doubt that "*the presence of steam is not essential to the ignition and explosion* of carbonic oxide and oxygen mixtures, as has been supposed hitherto,[6] but that the two gases can and do combine

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[*] Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 43.

[1] Research Associate, M.I.T. The greater part of this paper was written while the writer served as a National Research Fellow at Princeton University (1926-1928).

[2] Engler and Wild: Ber., **30**, 1669 (1897); Engler and Weissberg: "Kritische Studien uber die Vorgänge der Autoxydation," (1904). Bach: Compt. rend., **124**, 951 (1897); "Fortschritte d. naturw. Forsch." (Edited by Abderhalden), **1**, 85 (1910).

[3] Wieland: Ber., **45**, 484, 685, 679, 2603 (1912); **46**, 3327 (1913); **47**, 2085 (1914), and several other articles up to and including 1928.

[4] Meyer: Ber., **19**, 1089 (1886).

[5] Bone, Newitt and Townend: J. Chem. Soc., **123**, 2008 (1923); Bone, Fraser and Newitt: Proc. Roy. Soc., **110A**, 615 (1926); Bone and Townend: "Flame and Combustion in Gases," 340 (1927).

[6] The authors refer, in this case, to the early experiments of Dixon: British Association Reports, p. 503 (1880); Phil. Trans., **175**, 617 (1884); J. Chem. Soc., **49**, 384 (1886). These experiments have been recently cited by Adickes: Z. angew. Chem., **40**, 1131 (1927), as conclusive evidence in favor of Wieland's dehydrogenation theory.

directly without its intervention." Moreover, Lind[7] reports that under ionizing influence carbon monoxide combines with oxygên even at the temperature of liquid air and concludes that "reaction at this low temperature is a proof that moisture is not essential to the propagation of the ionic reactions." Similar conclusions have been reached by Dixon[8] in the case of the combustion of dry mixtures of cyanogen and oxygen, and by Baker[9] and by Dixon and Russell[10] in the case of the combustion of dry mixtures of carbon disulfide and oxygen. Furthermore, Mellor[11] states that extreme drying does retard the oxidation of phosphorus, but does not completely inhibit the process.

One finds equally striking chemical evidence in favor of the Engler-Bach theory in the successful attempts made recently to isolate "true" organic peroxides from auto-oxidation reactions. Clover[12] succeeded in isolating ether peroxide which, according to him, is responsible for the explosions occurring during distillations of ether. Jorissen and van der Beek[13] have recently prepared benzoperacid in relatively good yields by the auto-oxidation of benzaldehyde. Very recently Stephens[14] claims to have isolated a "true" peroxide of cyclohexene. while Mardles[15] succeeded in demonstrating the primary formation of extremely active and short-lived organic peroxides in the slow combustion of ethane. The experiments of Mardles are of special significance since they are at variance with the "hydroxylation theory"[16] of hydrocarbon combustion. Moreover, the very recent experiments of Milas[17] on the induced oxidations effected during the auto-oxidation of anethol, styrene, etc., demonstrate clearly the primary formation of unstable but very reactive peroxides.

Another source of evidence is to be found in the field of inhibition. The recent observations of Dhar,[18] Moureu and Dufraisse,[19] and others have shown that small quantities of certain inorganic as well as organic substances are capable of retarding or even preventing the oxidation of auto-oxidants, such as acrolein, benzaldehyde and sodium sulfite with molecular oxygen. Furthermore, Dixon[20] has observed that small quantities of ethylene and

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[7] Lind: "The Chemical Effects of Alpha Particles and Electrons" (Second Edition) 167 (1928).

[8] Dixon: J. Chem. Soc., **49**, 390 (1886).

[9] Baker: Phil. Trans., **179**, 582 (1888).

[10] Dixon and Russell: J. Chem. Soc., **75**, 600 (1899).

[11] Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **8**, 775 (1928).

[12] Clover: J. Am. Chem. Soc., **44**, 1107 (1922).

[13] Jorissen and van der Beek: Rec. Trav. chim., **45**, 245 (1926); van der Beek: **47**, 286 (1928).

[14] Stephens: J. Am. Chem. Soc., **50**, 568 (1928).

[15] Mardles: J. Chem. Soc., **1928**, 872.

[16] Bone and Townend: l.c. page 373.

[17] Milas: Proc. Nat. Acad. Sci., **14**, 844 (1928).

[18] Dhar: Proc. K. Akad. Wetensch., Amsterdam, **29**, 1023 (1921).

[19] Moureu and Dufraisse: Institut Internationale de Chimie Solvay, Bruxelles, April (1925), page 524; Chem. Reviews, **3**, 113 (1927).

[20] Dixon: Rec. Trav. chim., **40**, 305 (1925).

acetylene have a powerful inhibitory action on the phosphorescent combustion of carbon disulfide.

In the field of biology, Warburg[21] made the significant observation that small quantities of narcotic[22] or poisonous substances not only impede the respiration of living cells but inhibit it in a "reversible manner." Since the early work of Warburg important observations have been made in this field by Meyerhof,[23] Fleisch,[24] Szent-Gyorgyi,[25] and Wind.[26] On the basis of the foregoing experimental evidence, one may reasonably conclude that, with very few exceptions, one important criterion of auto-oxidations whether in gaseous, liquid or solid state,[27] *in vivo* or *in vitro*, is *their susceptibility to inhibitory action.* Wieland's theory is incapable of explaining these experimental facts since dehydrogenations are very little or not at all susceptible to inhibitory action.[28]

Still another source of evidence in favor of the "peroxide theory" is to be found in the fields of promoter action and induced oxidations. Thunberg[29] was the first to show that small quantities of iron salts produced startling effects on the auto-oxidation of lecithin. In this connection Warburg,[30] Meyerhof[31] and others have further demonstrated that iron salts are capable of accelerating auto-oxidations even in the living cell, while Spoehr[32] and Spoehr and Smith[33] have shown that sodium ferro pyrophosphate is an excellent oxygen carrier in inducing the oxidation of glucose and related sugars with atmospheric oxygen. This catalyst was found to induce not only the oxidation of reducing sugars but also that of sucrose and polyhydric alcohols which do not reduce Fehling's solution. The authors are not quite convinced as to the exact mechanism of their reactions but point out three possible ways whereby oxidations may occur, either by means of surface catalysis (adsorption), or by electronic oxidation and reduction of the catalyst, or by intermediate peroxide formation with the catalyst.

An important class of oxygen carriers which seem to play a very significant rôle in respiration phenomena of the living cell is that which includes compounds of the sulphydryl group which was first suggested by the work of

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[21] Warburg: Z. physiol. Chem., 69, 452 (1910); Erg. Physiol., 158, 190 (1914); Biochem. Z., 136, 266 (1923).

[22] Winterstein: "Die Narkose," 214, (1926) states that inhibition of auto-oxidations in the living cell should not be considered a specific action of narcotics and therefore is not the cause of narcosis.

[23] Meyerhof: "Chemical Dynamics of Life Phenomena," Chapter I (1924).

[24] Fleisch: Biochem. J., 18, 294 (1924).

[25] Szent-Gyorgyi: Biochem. Z., 150, 195 (1924); 157, 50, 298 (1925).

[26] Wind: Biochem. Z., 159, 58 (1925).

[27] Feldmann: Giorn. chim. ind. applicata, 9, 455 (1927).

[28] For a crucial test of Wieland's theory, see Tanaka: Biochem. Z., 157, 425 (1925); J. Oriental Med., 4, 4 (1925).

[29] Thunberg: Skand. Arch. Physiol., 24, 90, 94 (1910).

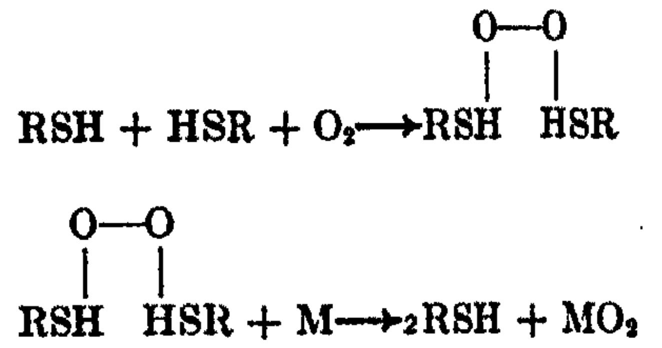
[30] Warburg: Biochem. Z., 142, 518 (1923); 145, 461 (1924); 152, 479 (1924).

[31] Meyerhof: l.c. pages 17-22.

[32] Spoehr: J. Am. Chem. Soc., 46, 1474 (1924).

[33] Spoehr and Smith: J. Am. Chem. Soc., 48, 236 (1926).

Heffter.[34] Glutathione[35] and thioglycollic acid[36] are two compounds of this group that have been extensively studied both *in vitro* and *in vivo*. Various mechanisms have been proposed to account for the ability of these compounds to transport oxygen to muscle tissue. Some biologists believe with Wieland that the sulphydryl group does not actually transport oxygen to the muscle tissue but instead removes hydrogen atoms from it. The assumption is made, therefore, that the disulfide which is formed by the spontaneous oxidation of sulphydryl acts as a hydrogen acceptor. That this mechanism is not plausible is clearly pointed out by Meyerhof who states that, "According to this theory (dehydrogenation) it remains, however, incomprehensible, how the sulphydryl compound can transport the oxygen in a larger amount and above all with greater speed than the disulfide." He then postulates a mechanism whereby oxygen may be transported to the muscle tissue by the sulphydryl:



$$RSH + HSR + O_2 \longrightarrow \begin{matrix} O & \!\!-\!\! & O \\ | & & | \\ RSH & & HSR \end{matrix}$$

$$\begin{matrix} O & \!\!-\!\! & O \\ | & & | \\ RSH & & HSR \end{matrix} + M \longrightarrow 2RSH + MO_2$$

where M represents the muscle tissue. Obviously this interpretation gives a more plausible explanation of the facts, but chemically it is highly improbable. More recently Kendall[37] suggested an interpretation of this process in which he made the assumption that the ability of glutathione and other analogous substances to transport oxygen to muscle tissue depends on the presence of "thermolabile unstable addition products containing oxygen and sulfur." Another interpretation of this process based on the recent advances of electronic structures is proposed later in this paper.

Auto-oxidations are not only susceptible to inhibitory and accelerating action of certain types of reagents, but are also capable of inducing the oxidation of other substances which ordinarily are not oxidised with molecular oxygen. As far back as 1890 Pedler[38] noticed the oxidation of atmospheric nitrogen during the combustion of carbon disulfide with air, while very recently Mardles[15] reports the induced oxidation of benzene, aniline, etc., during the slow combustion of ethyl ether or ethane. Furthermore, Feldmann[27] has recently shown that sodium amalgam induces the oxidation, with molecular oxygen, of mercury to mercuric oxide at 100°, also that of ethyl alcohol to acetic acid under pressure. Neither the mercury nor the alcohol alone are readily oxidized with oxygen under the conditions stated. The

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[34] Heffter: Med. nat. Arch., **1**, 81 (1908).

[35] Hopkins: Johns Hopkins Hospital Bull., **32**, 321 (1921); Biochem. J., **15**, 286 (1921).

[36] Meyerhof: l.c. pages 30-35.

[37] Kendall: Science, (2), **62**, 384 (1928).

[38] Pedler: J. Chem. Soc., **57**, 625 (1890).

present author[17] has further shown that during the auto-oxidation of anethol, styrene, etc., several substances like anthracene, phenanthrene, etc., are inducedly oxidized. All these substances have been shown to be quite inert to oxygen in the absence of the auto-oxidant. Therefore, one may safely conclude that another very important and quite general characteristic of auto-oxidations is their ability to induce the oxidation of other substances. In accordance with Wieland's view these reactions remain utterly incomprehensible.

The critics of the Engler-Bach theory have advanced the argument that organic peroxides alone, active though they may be, are not sufficiently strong oxidizing agents to oxidize either the muscle tissue or other comparatively inert organic substances. In order to test the justification of this criticism, the author performed the following experiment: Two g. of anthracene (Eastman Kodak, C.P. quality, free from anthraquinone) was suspended in 40 c.c. of glacial acetic acid contained in a 120 c.c. test tube and to the mixture was added 5 g. of benzoperacid.[39] The test tube with its contents was placed in an oil-bath kept at 110°C for one hour. The experiment yielded, besides other oxidation products of anthracene, 0.25 g. of anthraquinone. m.p. 281-283°C. This experiment seems to prove the inadequacy of the foregoing criticism. However, the peroxide theory, alone, cannot, in its present form, adequately explain the induced oxidations. Neither is it competent of explaining satisfactorily, in the opinion of the author, the retardation or acceleration effects produced on auto-oxidations by small quantities of certain types of chemical substances.

The New Interpretation

Granting that in all auto-oxidations oxygen adds in the molecular form, is there any new evidence to show how this addition might take place? This rather fundamental question may be answered satisfactorily only after a thorough and critical examination of the most recent views concerning the possible electronic configuration of oxygen on the one hand and of auto-oxidants on the other.

There seems to be a confusion, at present, as to the exact electronic configuration of molecular oxygen. On the basis of the paramagnetism of oxygen, one may conclude that the oxygen molecule which has a moment corresponding to two Bohr magnetons may be analogous to an atom with two electrons rotating in the same direction.[40] But all gaseous substances exhibiting paramagnetism consist of molecules possessing an "odd" number of electrons and oxygen therefore constitutes a distinct anomaly. To explain this anomaly Lewis[41] made the assumption that the predominant form of molecules in free oxygen is that in which each oxygen atom possesses an "odd" electron as, $:\underset{\cdot}{\ddot{O}}\ :\ \underset{\cdot}{\ddot{O}}:$. Accordingly Taylor and Lewis[42] thought that if such a

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[39] Houben-Weyl: "Die Methoden der organischen Chemie," 2, 113 (1922).

[40] Stoner: Phil. Mag., (7), 3, 336 (1927).

[41] Lewis: Chem. Rev., 1, 243 (1925).

[42] Taylor and Lewis: Proc. Nat. Acad. Sci., 11, 456 (1925).

molecule reacted with atomic chlorine, one of the "odd" electrons should either be transferred to the chlorine atom or be shared with it so that an inert configuration is formed around the chlorine atom. The remaining "odd" electron on the other oxygen atom should then impart paramagnetic properties to the chlorine dioxide molecule. This prediction was confirmed when the authors found that ClO_2 in CCl_4 was, indeed, paramagnetic. For a time, this evidence was quite convincing. Nevertheless, the anomaly still remains a mystery. Very recently Grimm[43] proposed an electronic structure for ClO_2 analogous to that of NO_2,

$$:\overset{..}{\underset{..}{O}}:\overset{.}{\underset{..}{Cl}}:\overset{..}{\underset{..}{O}}: \qquad :\overset{..}{\underset{..}{O}}:\overset{.}{N}:\overset{..}{\underset{..}{O}}:$$

Although Grimm's structure may account for the paramagnetic properties of ClO_2, it fails to explain the radical difference in chemical properties between the two gases. Strange to say, both Lewis and Grimm failed to consider other possible structures. Therefore, if we make the following assumption that *in all auto-oxidations* (oxidations in which oxygen reacts in the molecular form) *the atoms to which the oxygen molecule initially adds may be regarded as making definite contributions of two electrons to it,* in the case of the chlorine atom, the following electronic structure of chloride dioxide may be deduced,

$$\cdot\overset{..}{\underset{..}{Cl}}: \;+\; \overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}: \qquad \cdot\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}::$$

This, then, may be termed "dative" peroxide[44] of chlorine. It seems to explain not only the paramagnetic properties of the gas, but also its instability and explosive nature under the influence of light or heat. In accordance with this reasoning, we are justified to conclude that molecular oxygen reacts by sharing two electrons with other molecules to form metastable or dative peroxides[45] which are characterized with high instability and energy content. Owing to their high instability, these peroxides may either revert instantaneously to the ordinary peroxides by transferring their excess energy to other molecules, or initiate the oxidation of other molecules.

Molecular Valence Electrons

On the basis of the reasoning in the preceding section, it may be inferred that auto-oxidations can occur only when the auto-oxidant possesses unshared or "exposed" electrons comparable to valence electrons of the various

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[43] Grimm: "Handbuch der Physik," **24**, 513 (1927).

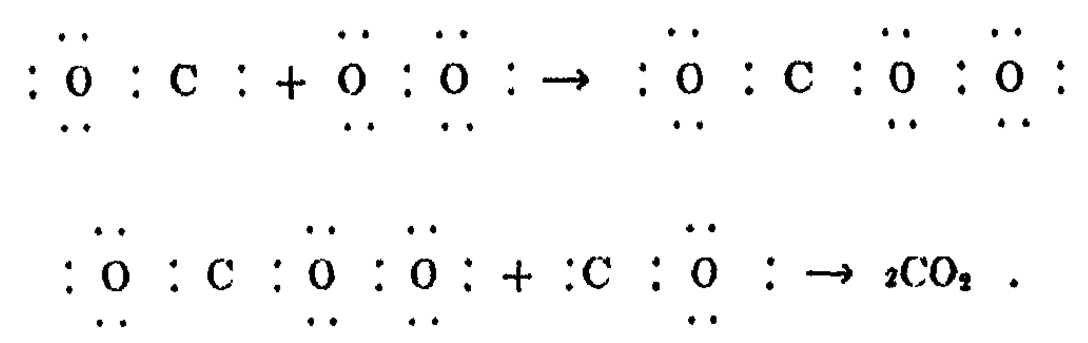
[44] The term "dative" has been first suggested by Menzies: Nature, **121**, 457 (1928), to denote a type of covalency in which one of the atoms in the "dative" bond contributes both electrons.

[45] It is best here to point out that in developing this view of auto-oxidations, I have derived considerable benefit from the recent views of Sidgwick: J. Chem. Soc., **123**, 725 (1923); "The Electronic Theory of Valence," 116 (1927).

[46] Shared electrons which can be easily "exposed" by absorption of some form of external energy.

elements.[47] In view of the recent developments in connection with electronic bands, Mulliken[48] and Birge[49] have shown that the energy levels associated with valence electrons of molecules are analogous in all essential aspects with the valence electrons of atoms. In other words, molecular valence electrons are capable of existence in a series of electronic states. In molecules like CO, for example, it is assumed that each atom retains its own K electrons, and of the outer ten electrons, eight form some sort of a firmly bound symmetrical group, while the remaining two are more loosely bound and therefore give rise to a set of energy levels which are analogous to those attributed to valence electrons in atoms. These two electrons which constitute a "lone" or unshared pair, are termed "molecular valence electrons."

Now, if the view expressed in the early part of this section is correct, one would naturally expect CO to combine with one molecule of oxygen to form an unstable and highly reactive dative peroxide which will further react with another molecule of CO to form two molecules of CO_2, as



$$:\underset{\cdot\cdot}{\ddot{O}}:C: + \underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}: \rightarrow :\underset{\cdot\cdot}{\ddot{O}}:C:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:$$

$$:\underset{\cdot\cdot}{\ddot{O}}:C:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}: + :C:\underset{\cdot\cdot}{\ddot{O}}: \rightarrow 2CO_2 .$$

The explosive nature of this reaction, as noted by Bone and his students,[5] indicates clearly the possibility of an intermediate metastable peroxide formation.

This view may be extended further to include unshared electrons found in molecules like NO, NH_3, PH_3, SO_2, PHSOX, NH_2NH_2, H_2S, HI and those containing unsaturated linkages. All these substances are auto-oxidized, although under different conditions, a fact which seems to indicate that the molecular valence electrons are at different "penetration" levels depending upon the "promotion energies," the effective nuclear charge of the parent atom[50] and the stability of the "unpromoted" shared electrons in the auto-oxidant molecule. For example, NH_3 reacts with O_2 only at relatively high temperatures, while PH_3 burns spontaneously in O_2 even at the temperature of solid CO_2. This difference in reactivity between NH_3 and O_2 and PH_3

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[47] Since the writing of the present paper, a very important article has been published by Mulliken: Phys. Rev., 32, 186 (August 1928), in which the writer uses the term "promoted" electrons to denote electrons whose *n* values (principal quantum numbers) have been increased as a result of atomic combinations and the formation of molecules.

[48] Mulliken: Phys. Rev., (2) 26, 561 (1925); Proc. Nat. Acad. Sci., 12, 144, 338 (1926).

[49] Birge: Bull. Nat. Res. Council, 11, part III, 69 (1926).

[50] Latimer and Rodebush: J. Am. Chem. Soc., 42, 1419 (1920).

and O_2 indicates not only that the two molecules have different degrees of "penetration" of molecular valence electrons but also a difference in energy content of the more firmly bound electrons.

But is there any chemical evidence to show that molecular oxygen combines initially with substances containing molecular valence electrons? From the auto-oxidation of $(C_2H_5)_3P$, Jorissen[51] succeeded in isolating $(C_2H_5)_3PO_2$, the peroxide properties of which have been demonstrated by Engler and Wild.[52] Moreover, one might expect that the "blocking" of molecular valence electrons by other atoms would make the molecule more inert to oxygen. This is actually found to be the case with several substances. In Table I, the compounds listed under Column I are readily oxidized with oxygen, while their salts listed in Column II are relatively stable in oxygen.

TABLE I

Substances easily oxidized	Substances stable in oxygen
$H_3P{:}$[53]	$H_3P{:}H\ I$
$(C_2H_5)_3P{:}$[51]	$(C_2H_5)_3P{:}C_2H_5\ Br$
$(C_2H_5)_3Sb{:}$[54]	$(C_2H_5)_3Sb{:}C_2H_5\ Br$
$(CH_3)_3As{:}$[55]	$(CH_3)_3As{:}CH_3\ Br$
$\overset{..}{N}H_2\overset{..}{N}H_2$[56]	$NH_2NH_2(H_2SO_4)_2$
$R\overset{..}{N}H\overset{..}{N}H_2$[57]	$RNH\ NH_2H_2SO_4$
$Ar\overset{..}{N}HOH$[58]	$ArNHOH\ H_2SO_4$

In addition to these substances several aryl amines, hydrazones, etc., well known to organic chemists, are isolated only in the form of their salts. In accordance with the view presented in the foregoing pages, one would expect the substances on the right hand column of Table I to react with oxygen by virtue of their molecular valence electrons. Since the degree of reactivity of these substances with oxygen is known only qualitatively at present, we cannot draw any definite conclusion other than to state that the molecular valence electrons present in these substances may be insufficiently "energized" to initiate reaction with oxygen under ordinary conditions.

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[51] Jorissen: Ber., **29**, 1707 (1896).

[52] Engler and Wild: Ber., **30**, 1673 (1897).

[53] Olschewsky: Monatshaft, **1**, 372 (1886).

[54] Christiansen: "Organic Derivatives of Antimony," p. 25 (1925).

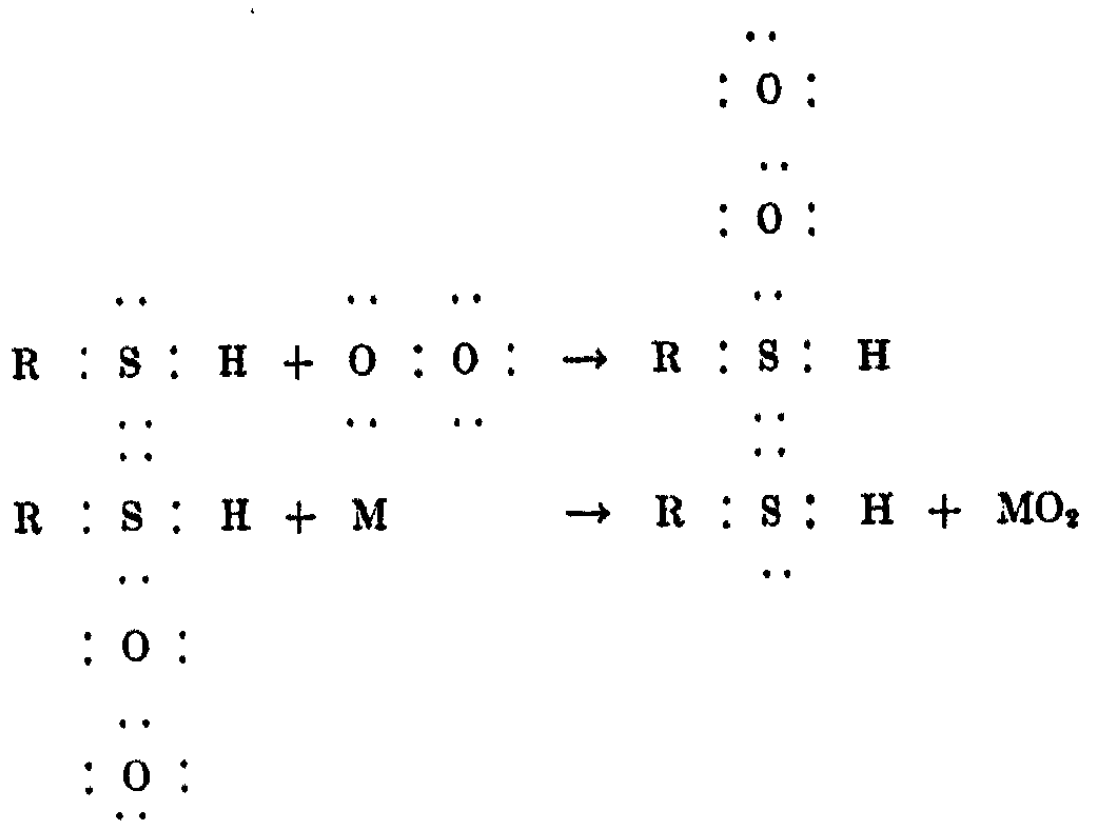
[55] Raizis and Gavron: "Organic Arsenical Compounds," p. 66 (1923).

[56] Cuy and Bray: J. Am. Chem. Soc., **46**, 1786 (1924).

[57] Chattaway: J. Chem. Soc., **91**, 1323 (1907).

[58] Bamberger: Ber., **27**, 1551 (1894); **33**, 118 (1906).

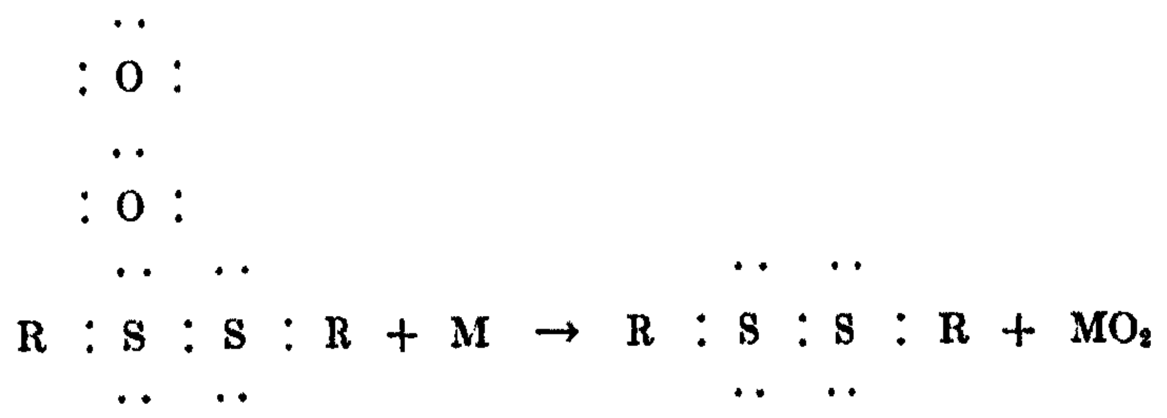
We are now in a position to explain the ability of sulphydryl groups to transfer "active" oxygen to muscle tissue or to other organic substances.



$$R:\overset{..}{\underset{..}{S}}:H + \overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}: \rightarrow R:\overset{:\ddot{O}:}{\overset{:\ddot{O}:}{\underset{..}{\overset{..}{S}}}}:H$$

$$R:\underset{\underset{:\ddot{O}:}{\underset{:\ddot{O}:}{..}}}{\overset{..}{S}}:H + M \rightarrow R:\overset{..}{\underset{..}{S}}:H + MO_2$$

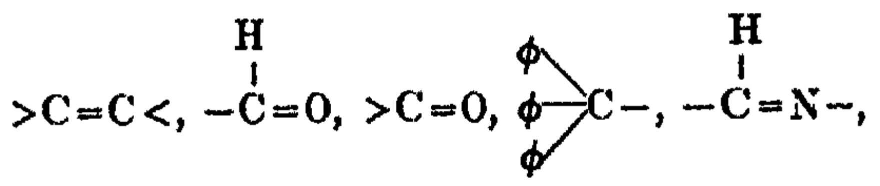
Similarly, the ability of the disulfide to transfer the oxygen may be explained:



$$R:\overset{:\ddot{O}:}{\overset{:\ddot{O}:}{\underset{..}{\overset{..}{S}}}}:\overset{..}{\underset{..}{S}}:R + M \rightarrow R:\overset{..}{\underset{..}{S}}:\overset{..}{\underset{..}{S}}:R + MO_2$$

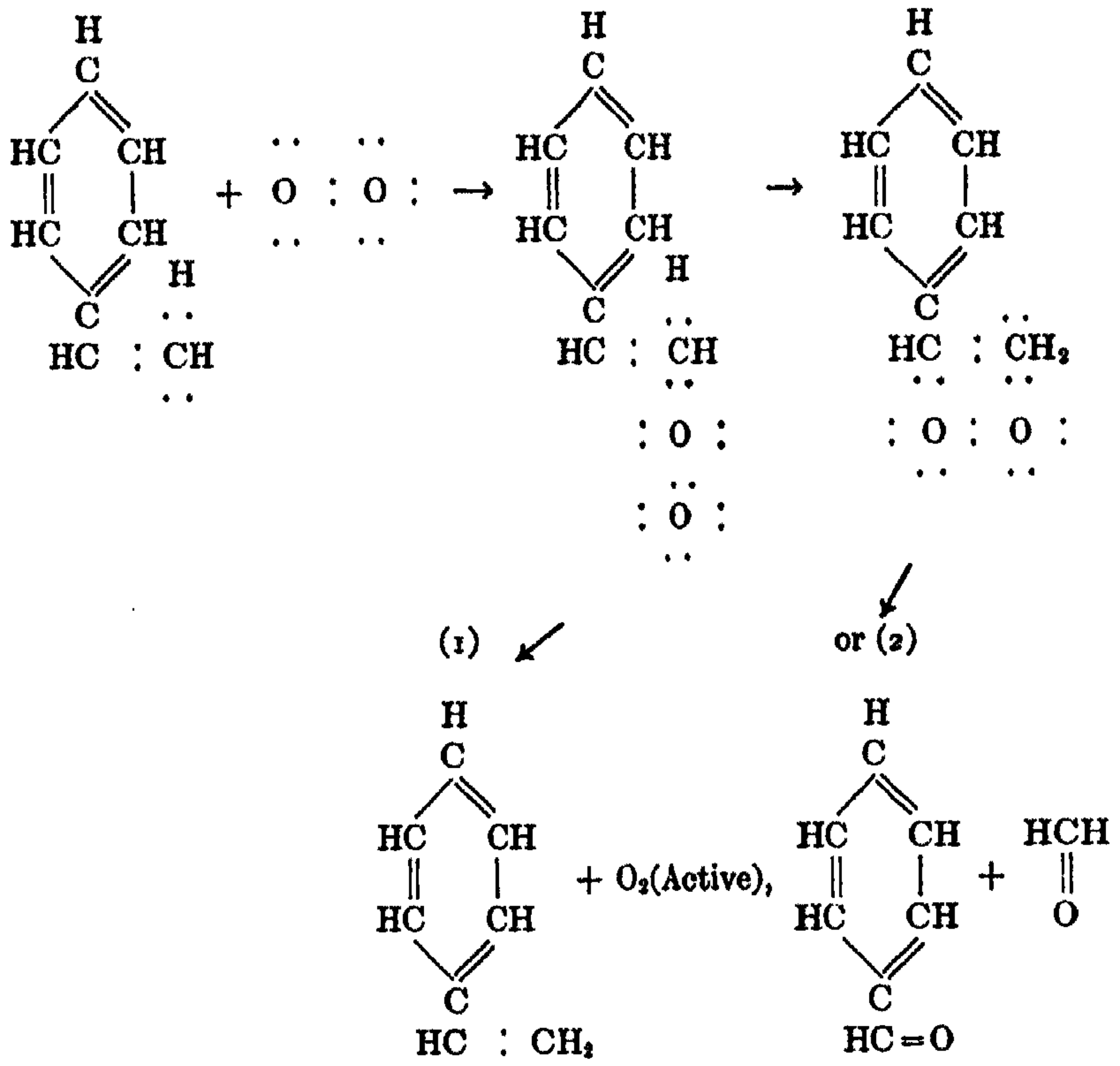
However, the "penetration" of molecular valence electrons in the disulfide is much greater, due to a considerable liberation of energy during its formation from the sulphydryl, and therefore it would be expected to be a poorer oxygen carrier.

The absorption of molecular oxygen by unsaturated groups like $-C\equiv C$,



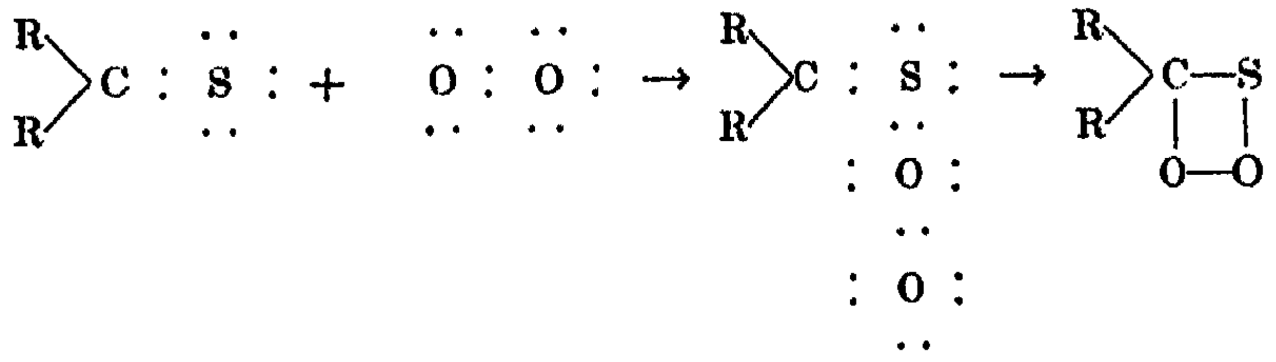
$>C=C<$, $-\overset{H}{\overset{|}{C}}=O$, $>C=O$, $(\phi)_3C-$, $-\overset{H}{\overset{|}{C}}=N-$, $>C=S$, etc., to form dative peroxides may be best illustrated by the following two typical examples:

(1) Auto-oxidation of Styrene:—



In the first case the active oxygen will oxidize other substances inert to molecular oxygen. Of course, the aldehydes formed during the second course of the reaction oxidize further to the corresponding acids.

(2) Auto-oxidation of Sulfones:—Delépine[59] observed the formation of ketones and sulfur trioxide in addition to small quantities of sulfur dioxide and sulfur. The main reaction may be expressed as follows:



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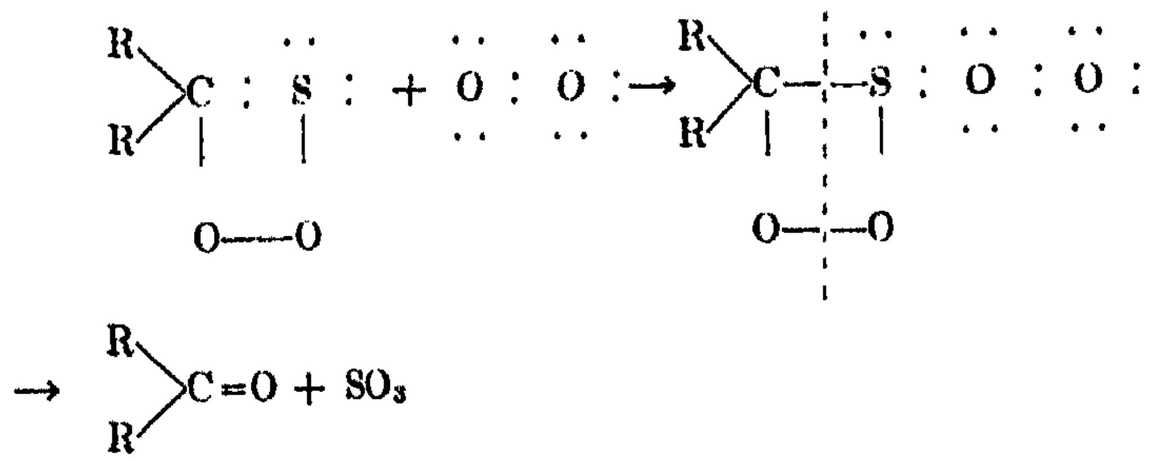
[59] Delépine: Bull., 31, 762 (1922).



(2)

Side reactions are also likely to occur, due, perhaps, to the interaction of SO_3 with the original sulfone molecules. If the mechanism, as shown above, is correct, the double dative peroxide represented in the second reaction, would possess much more energy than would a single dative peroxide. This is borne out by the results of Delépine who observed that during the spontaneous auto-oxidation of sulfones considerable visible radiation is produced. The spontaneous auto-oxidation of yellow phosphorus may be analogously interpreted.

Inhibition and Acceleration of Auto-Oxidations

In the interpretation of band spectra, modern spectroscopists have arrived at the conclusion that the total energy of a molecule is made up of the energy due to the transitions of electronic orbits, the oscillatory energy of nuclear vibrations and the rotational energy of the molecule as a whole. Since the molecular valence electrons are more loosely bound to the molecule, they may be assumed to be more easily affected by environmental disturbances, such as collisions from neighboring molecules or electrons, radiation and temperature effects. Therefore, *the first change which may occur in any chemical reaction is the change of electronic energy caused by environmental forces.* This change causes an immediate change in the vibrational and rotational energies of the molecule in order that equilibrium may be established.

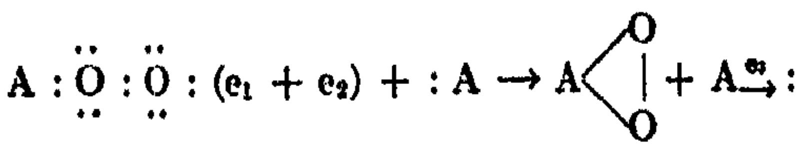
Arrhenius was the first to point out that molecules should be in an "activated" state before they can take part in any chemical reaction. In the case of auto-oxidants, the "activation" or the "de-activation" of molecules may be governed by the following energy considerations: (1) The existence of activated molecules depends upon the "penetration" of molecular valence electrons. Penetration may be defined as the energy level of the molecular valence electrons at a definite equilibrium state of the molecule in question. (2) The energy transfer among molecules under ordinary conditions is manipulated entirely through changes of the loosely bound molecular valence electrons.

If A: represents a molecule of an auto-oxidant and e_1 the energy of activation, the changes which may occur during the auto-oxidation of the molecule A: may be represented as follows:

$$A: + e_1 \rightarrow A \xrightarrow{e_1}: \qquad (1)$$

$$A\xrightarrow{e_1}: + \ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}: \rightarrow A:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:(e_1 + e_2) \qquad (2)$$

where e_1 is the energy due to the instantaneous neutralization of the activated molecule $A \overset{e_1}{\rightarrow} :$ and O_2. Furthermore, the electrons which are directly responsible for the formation of the dative peroxide shown in (2) have undergone an increase in their principal quantum numbers due to the absorption of energy e_2. Molecules containing these electrons would be characterized with a very low energy of dissociation and extremely high instability. Mere collisions with other molecules therefore will suffice to effect a rearrangement or even decomposition of the dative peroxide with liberation of energy. This energy, according to Christiansen[60] is utilized to initiate reaction chains.



$$A : \ddot{\underset{..}{O}} : \ddot{\underset{..}{O}} : (e_1 + e_2) + : A \rightarrow A\langle O_2 + A \overset{e_3}{\rightarrow} : \qquad (3)$$

where e_3 is the sum of $e_1 + e_2$. This energy increases with each subsequent reaction chain and eventually, according to Semenoff,[61] leads to explosive reactions.

If an inhibitor collided with the dative peroxide, all the excess energy of the latter would be completely absorbed by the molecular valence electrons of the former, thus the initiation of new reaction chains is prevented and the rate of auto-oxidation is greatly reduced. A critical examination of the various inhibitors of auto-oxidation reveals the fact that all of them possess molecular valence electrons, but probably at different penetrations. An exchange of energy, therefore, between the inhibitor and the dative peroxide resulting in the partial activation of the former, is inevitable to inhibitory action. Moreover, this exchange of energy takes place instantaneously either by electronic impacts or by emission and re-absorption of invisible radiation. The activated molecules of the inhibitor can then be either oxidized by the organic peroxides or by free oxygen,[62] or combine with the active auto-oxidant molecules forming unstable complexes which may decompose to yield the original inhibitor molecules. Anthraquinone, for example, was found by the author to inhibit the auto-oxidation of anethol yet it was recovered unchanged at the end of the reaction.[63]

The mechanism of the promoter action on auto-oxidations, on the other hand, can be explained by assuming that the valence electrons of the promoter transfer their energy to the inactive auto-oxidant either directly or through the formation of an intermediate dative peroxide of the promoter.

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[60] Christiansen: J. Phys. Chem., 28, 145 (1924).

[61] Semenoff: Z. physik, 48, 571 (1928).

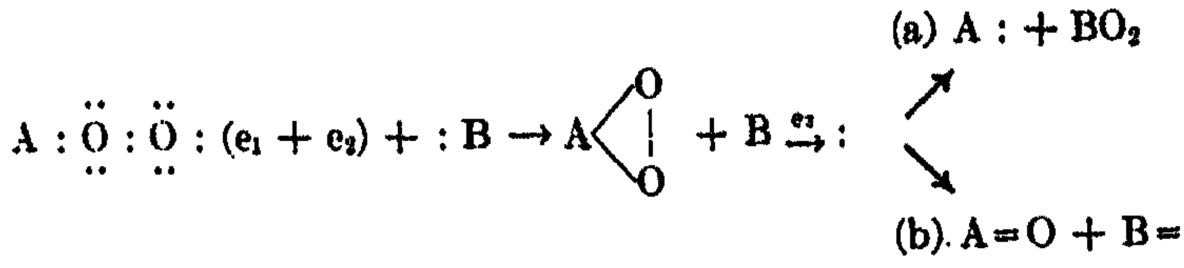
[62] Bäckström: Medd. K. Vetenskapsakad. Nobel-Inst., 6, 38 (1927).

[63] Milas: Proc. Nat. Acad. Sci., July (1929).

Schematically, the inhibitory and accelerating action produced by small quantities of substances on auto-oxidations and the induced effect of the latter may be explained as follows:

$$A : + e_1 \longrightarrow A\overset{e_1}{\rightarrow} : \qquad (1)$$

$$A\overset{e_1}{\rightarrow} : + \underset{\cdot\cdot}{\ddot{O}} : \underset{\cdot\cdot}{\ddot{O}} : \longrightarrow A : \underset{\cdot\cdot}{\ddot{O}} : \underset{\cdot\cdot}{\ddot{O}} : (e_1 + e_2) \qquad (2)$$



(3)

Reaction (b) is irreversible, while (a) might under favorable conditions, reverse itself.

In the case of the promoter action, the following scheme may be adopted:

$$A: + C\overset{e_1}{\rightarrow} : \longrightarrow A\overset{e_1}{\rightarrow} : + C : \text{(Promoter action)} \qquad (4)$$

or

$$C\overset{e_1}{\rightarrow} : + \underset{\cdot\cdot}{\ddot{O}} : \underset{\cdot\cdot}{\ddot{O}} : \longrightarrow C : \underset{\cdot\cdot}{\ddot{O}} : \underset{\cdot\cdot}{\ddot{O}} : (e_1 + e_2),$$

and

$$C : \underset{\cdot\cdot}{\ddot{O}} : \underset{\cdot\cdot}{\ddot{O}} : (e_1 + e_2) + : A \longrightarrow C : + AO_2 + e_1 + e_2$$

or

$$\text{''} \qquad + A\overset{e_1}{\rightarrow} : \longrightarrow C : + AO_2 + 2e_1 + e_2 \qquad (5)$$

Reaction (5) shows promoted + induced oxidation. In the above scheme B represents the inhibitor and C the promoter.

As a concluding remark, it may be stated that the new interpretation of auto-oxidation reactions, as presented in the foregoing pages, though it differs from any views so far presented serves, in the opinion of the author, as a compromise among the prevalent, widely different views held by the various investigators in the field.

Research Laboratory of Organic Chemistry,
Massachusetts Institute of Technology,
Cambridge, Mass.
March 30, 1929.

THE SHAPES OF DROPS, AND THE DETERMINATION OF SURFACE TENSION

B. B. FREUD AND W. D. HARKINS[*]

Introduction

While the surface tension of a liquid may be determined with considerable accuracy by the drop weight method, provided the empirical correction curve of Harkins and Brown[1] is used, the surface tension thus obtained is based fundamentally upon capillary height determinations as made by them. The apparently well-justified assumption which they used is that the correction factor is determined entirely by the shape of the drop. Their method is frankly empirical in regard to the relation between the size of the drop and the known constants of liquid and tip, although the comparison between drops of different liquids is supported by theory. The present study was undertaken in the hope of supplying a theoretical basis for the empirical relations just noted. Although this hope has not been realized, other relationships have come to light.

The problem is the study of the changes taking place when a drop of liquid falls from a circular horizontal tip. It has been found convenient to consider it under the topics, the hanging, the detaching, and the detached drop. It is necessary to simplify further by assuming that the liquid has a very small viscosity, or that sufficient time is allowed to permit the system to come to equilibrium. The second alternative does not of course apply to the detaching drop as in this case the time changes are not under our control. The starting point for the investigation must be the initial state, that is, the drop which has not yet become unstable and started to separate,—what we have termed the hanging drop.

The Hanging Drop

The shapes of liquid surfaces have been discussed mathematically by many authors, and are expressed by the familar equation of Laplace:

$$p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (1)$$

where p indicates the pressure at any point of the surface, R_1 and R_2 the principal radii of curvature of the surface at that point, and γ the surface tension of the liquid. The special form of it applicable to surfaces of revolution is:

$$\frac{y''}{(1 + y'^2)^{3/2}} + \frac{y'}{x(1 + y'^2)^{1/2}} = \frac{2}{a^2}(h-y) \quad \text{or} \quad \frac{du}{dx} + \frac{u}{x} = \frac{2}{a^2}(h-y) \qquad (2)$$

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[*] Kent Chemical Laboratory, The University of Chicago, Chicago, Illinois.

[1] Harkins and Brown: J. Am. Chem. Soc., 41, 499 (1919).

where R_1 and R_2 have been replaced by their equivalents $\frac{y''}{(1+y'^2)^{3/2}}$ and $\frac{y'}{x(1+y'^2)^{1/2}}$, x and y being the coordinates of the point measured from the bottom of the drop as origin and the axis of symmetry of the drop as y-axis, y'' and y' the second and first derivatives of y with respect to x respectively, and u the sine of the angle the tangent to the profile (the boundary of a vertical section of the drop through the axis) makes with the horizontal. For p/γ has been substituted $2(h-y)/a^2$. The factor $(h-y)$ is the height of the column of the liquid which would exert the pressure p at the given point. If the pressure of the atmosphere outside the drop and on the liquid surface inside the tip is the same, and if this surface is not so small as to show the effects of a capillary rise, then $(h-y)$ is the head of the liquid above the given point, and h is the head above the origin. By definition $2/a^2$ is equal to gd/γ. It should be noted that we are following the German custom, instead of that of certain English writers who make $a^2 = \gamma/gd$.

There are other ways of obtaining the same equation, of which the simplest[1] is that of equating the forces acting on a horizontal section of a drop, as follows:

$$2\pi\, xu\gamma = Vgd + \pi x^2\,(h-y)gd \qquad (3)$$

$$V = \int_0^y \pi x^2 dy = \pi xua^2 - \pi x^2(h-y)$$

V is the volume of the liquid below the section we are considering. It will be seen that the surface tension around the section holds up the weight of the liquid below it and a column of liquid $(h-y)$ in height and of base equal to the area of the section itself. Differentiation of this equation yields Equation (2) and conversely integration of that expression yields this.

Quite different premises will also give this expression. The shapes of soap bubbles have been developed by the calculus of variations. The problem in that case is to find the smallest surface enclosing a given volume. A similar treatment of our problem, with the additional condition that the center of gravity must be in a given position, yields the above expression. The additional symbols required are r, the radius of the tip (a particular value of x), and c, the distance of the center of gravity from the origin. We must consider the three integrals:

$$V = \int_0^r \pi x^2 y' dx$$

$$Vc = \int_0^r \pi x^2 y y' dx$$

$$S = \int_0^r 2\pi x(1+y'^2)^{1/2} dx$$

The procedure is to let the form of the function $y = f(x)$ (which is not known to us) change so that x and y remain constant, but y' changes by an amount $\delta y'$. The corresponding change in V is δV. Then

$$V + \delta V = \int_0^r \pi x^2 (y' + \delta y')dx = \int_0^r \pi x^2 y' dx + \int_0^r \pi x^2 \delta y' dx \qquad (4)$$

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[1] Worthington: Proc. Royal Soc., 32, 363 (1881); Rayleigh: Phil. Mag., (5) 48, 321 (1899).

Cancelling V and its equivalent in Equation (4), and substituting $\frac{d}{dx}(\delta y)$ for $\delta y'$,

$$\delta V = \int_0^r \pi x^2 \frac{d}{dx}(\delta y) = \pi x^2 \delta y\Big]_0^r - \int_0^r 2\pi x \delta y dx$$

The same reasoning applied to Vc and S yields:

$$\delta(Vc) = \pi x^2 y \delta y\Big]_0^r - \int_0^r 2\pi xy\delta y dx$$

$$\delta S = \frac{2\pi xy'}{(1 + y'^2)^{1/2}}\delta y\Bigg]_0^r - \int_0^r \frac{2\pi y'}{(1 + y'^2)^{1/2}}\delta y\, dx - \int_0^r \frac{2\pi xy''}{(1 + y'^2)^{3/2}}\delta y\, dx$$

It is a principle of the calculus of variations that if two integrals are to be held constant and a third maximized or minimized, and if the expressions left under the integral signs, after the variations of y' and of higher derivatives have been reduced to δy as above (exclusive of $\delta y dx$), be f_1, f_2, and f_3, then

$$f_1 + mf_2 + nf_3 = 0$$

where m and n are constants. Applying this to our problem, we obtain the expression:

$$2\pi x + 2\pi mxy + \frac{2\pi ny'}{(1 + y'^2)^{1/2}} + \frac{2\pi nxy''}{(1 + y'^2)^{3/2}} = 0$$

This can be easily transformed into Equation (2), with m/n in the place of $2/a^2$ and $-1/m$ in that of h. At the bottom of the drop $p_0 = hgd$. As h in the old notation equals $-1/m$ in the new, $m = -gd/p_0$. Accordingly, $n = -\gamma/p_0$.

It seems to be impossible to integrate Equation (2), and so find directly the functional relation between y and x, or even to integrate it once and obtain the relation between y', y and x. It can, however, be integrated in series, by the use of Taylor's theorem, as has been described by Runge[1] and by Lohnstein.[2] The two constants, a and h, may be reduced to one by the substitution of $a\bar{x}$, $a\bar{y}$, $a\bar{h}$ and $a^3\bar{V}$ for x, y, h, and V respectively, enabling us to use one series of curves to express the results for all liquids.[3] Fig. 1 shows the drop profiles for values of h ranging from 0 to 4. It will be seen that they are of two kinds of profiles: in one $\bar{y}$ continuously increases with $\bar{x}$, and in the other there are one or more constrictions, which we shall call necks. If a constant-$\bar{x}$ (iso-$\bar{x}$) line is followed from the $\bar{x}$-axis to Curve I, Fig. 1, (the meaning of which will be explained later), the portion of the curves between that iso-$\bar{x}$ line and the $\bar{y}$-axis shows the successive profiles of the drop as the volume increases.

Beyond the point on the iso-$\bar{x}$ line where Curve I crosses it, the volume calculated from Equation (3) no longer increases, and we shall therefore call this the curve of maximum volume. Fig. 2 shows more clearly the increase

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[1] Runge: Math. Ann., **46**, 175 (1895).

[2] Lohnstein: Ann. Physik, (4) **20**, 237, 606 (1906); **21**, 1032; **22**, 767 (1907).

[3] Bashford and Adams have published data on hanging as well as on sessile drops. "Capillary Action," Cambridge University Press, (1883).

of $\bar{V}$ with increasing $\bar{h}$ until a maximum is reached, after which $\bar{V}$ decreases. The procedure in the usual drop weight measurement is to increase slowly the volume of the drop until finally it falls. Lohnstein's conclusion was that the point where the volume can no longer be increased marks the limit of

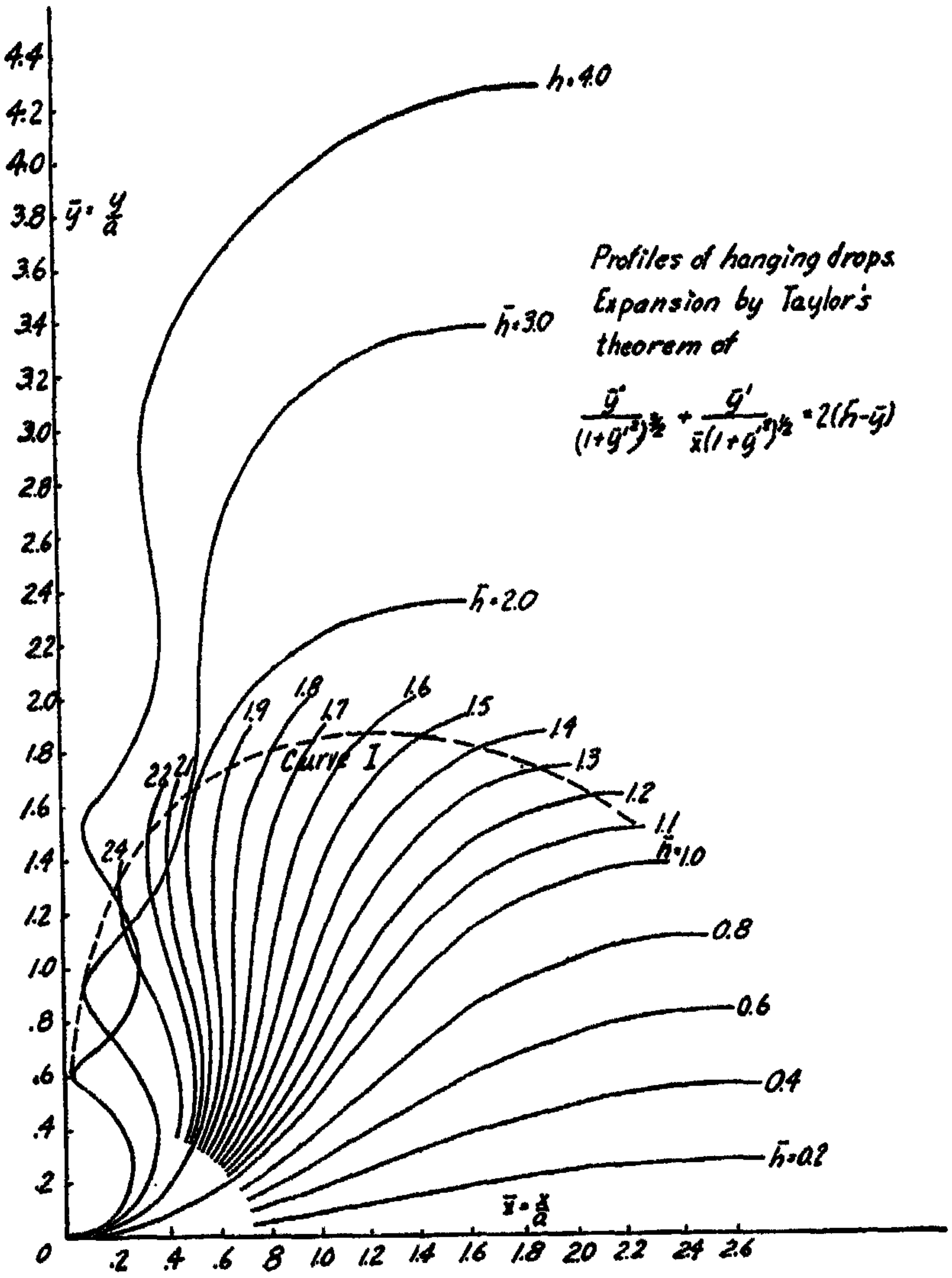

FIG. 1

stability of the drop, which seems entirely reasonable. In other words, the profile below the curve of maximum volume shows the shape of the drop at the moment before it begins to detach. These drop profiles must be the starting-point of any satisfactory theory of drop-weights.

Table I

Significant Points of Fig. 1

$\bar{h}$	$\bar{u} = 1$ at		$\frac{d\bar{u}}{d\bar{x}} = 0$ at		Drop of Maximum Volume		
	$\bar{x}$	$\bar{y}$	$\bar{x}$	$\bar{y}$	$\bar{x}$	$\bar{y}$	$\bar{V}$
.2			1.250	.130			
.4			1.269	.272			
.6			1.233	.407			
.8			1.180	.538			
1.0			1.112	.665			
1.1			1.070	.726	2.28	1.51	6.68
1.2			1.025	.785	2.05	1.63	6.50
1.3			.973	.841	1.86	1.73	6.06
1.4			.918	.894	1.67	1.82	5.73
1.5			.858	.941	1.39	1.835	4.44
1.6			.795	.983	1.22	1.868	3.70
1.7			.727	1.016	.98	1.828	2.82
1.8	.658	1.041	.658	1.041	.81	1.800	2.20
1.9	.602	.790	.589	1.077	.66	1.759	1.71
	.576	1.310					
2.0	.560	.692	.522	1.054	.517	1.654	1.28
	.485	1.402					
2.1	.524	.626	.460	1.041	.418	1.601	1.005
	.399	1.423					
2.2	.495	.575	.417	1.020	.330	1.500	.787
	.323	1.402					
2.4	.446	.500	.311	.958	.213	1.300	.512
	.213	1.284					
3.0	.346	.369	.168	.756	.078	.920	.205
	.078	.916	.190	1.094			
			.538	2.073			
4.0	.255	.264	.084	.547	.026	.610	.074
	.026	.609	.086	.673			
	.284	1.016	.154	1.346			
	.081	1.504	.170	1.678			
	.382	2.258	.349	2.582			
	.317	2.890					

Fig. 3 shows not $\bar{V}$ but $\bar{V}/\pi\bar{x}$, which is called ϵ, plotted against $\bar{x}$. A maximum $\bar{V}$ for a particular $\bar{x}$ of course means a maximum ϵ also, and so the envelope of this series of curves may also be used for the determination of the curve of maximum volume. As it is somewhat easier to read the points of contact of the curves with the envelope on this set of curves than on those of Fig. 2, it has been used to obtain the values of the maximum volumes of this paper. It must be said, however, that these are the most inaccurate data in the paper because of this difficulty in reading the exact point of contact.

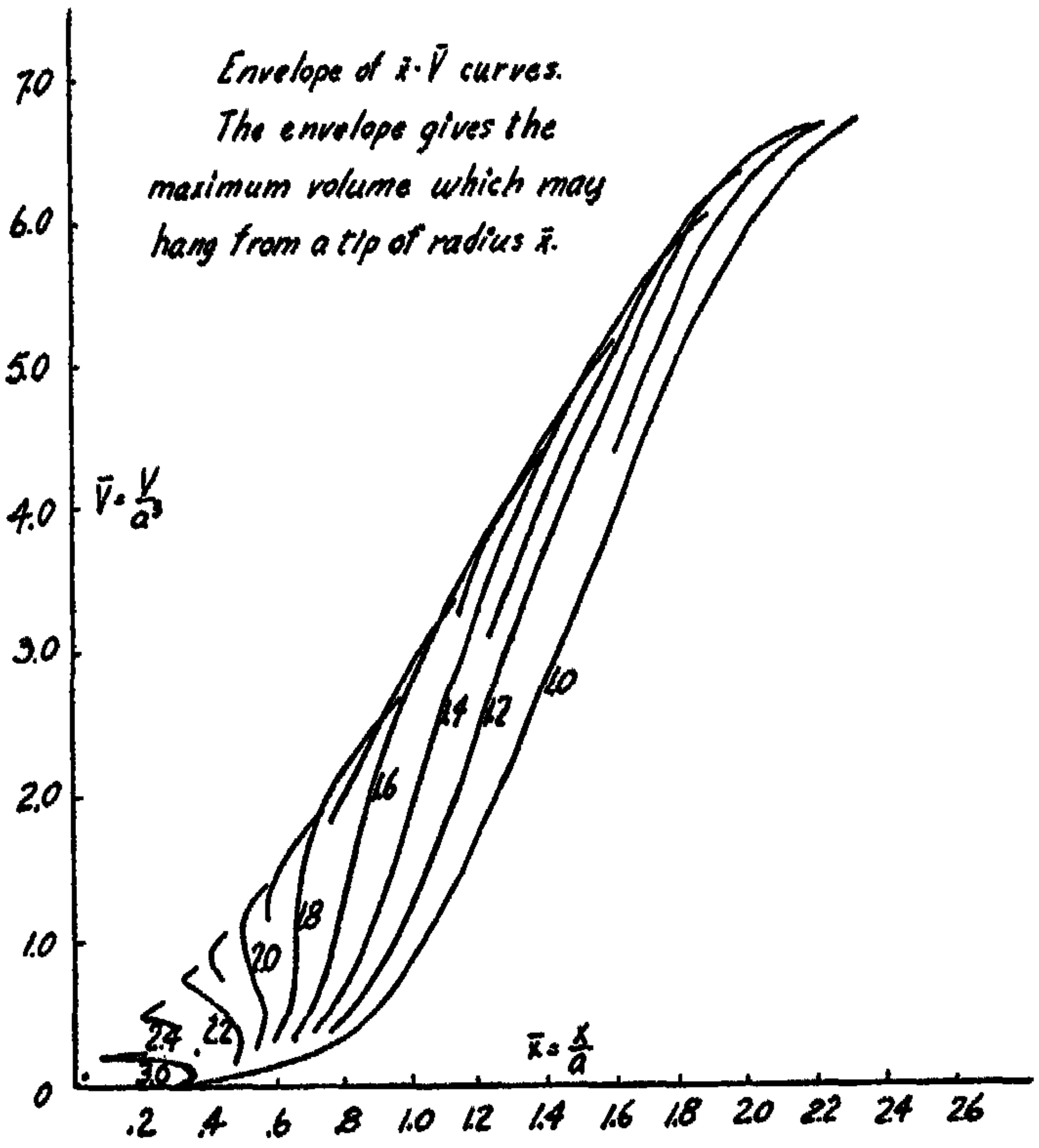
Envelope of x̄-V̄ curves.
The envelope gives the
maximum volume which may
hang from a tip of radius x̄.
V̄ = V/a³
x̄ = x/a
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
3.0
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0

FIG. 2

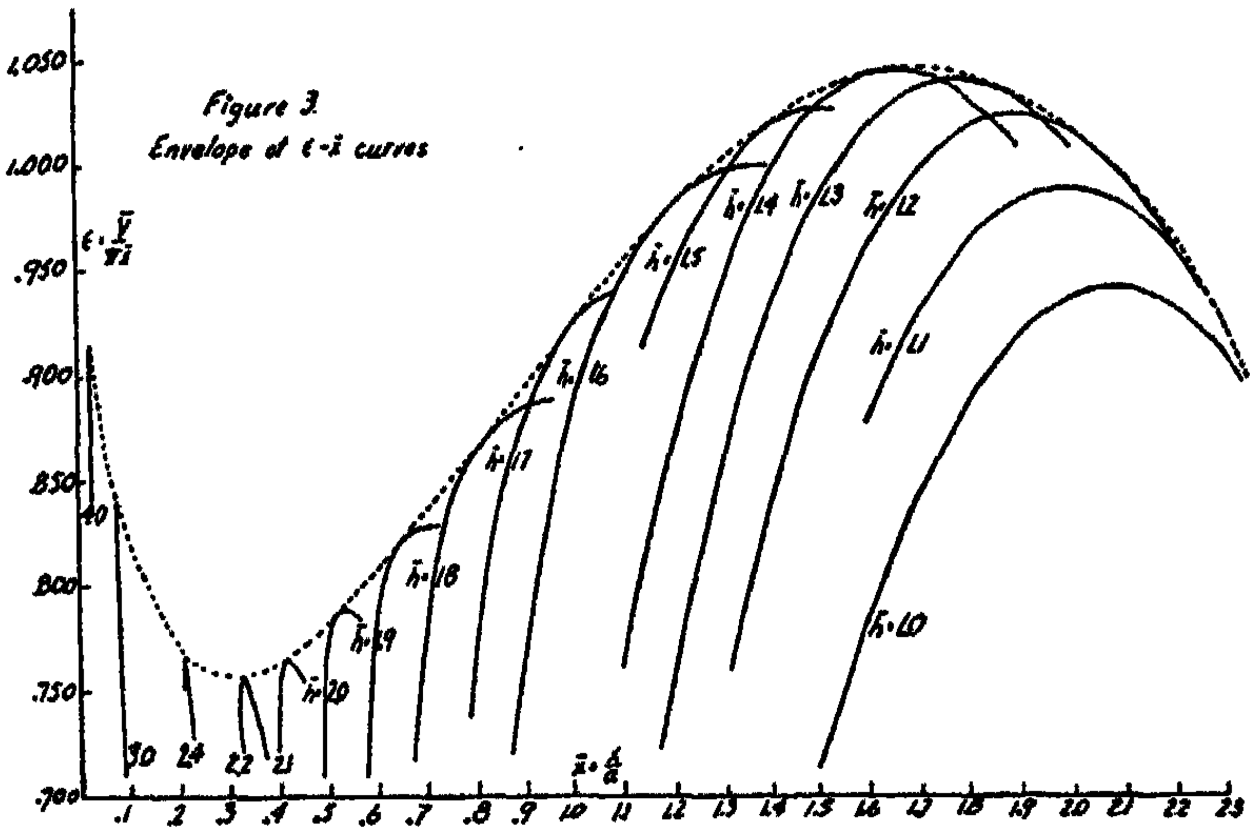
Figure 3
Envelope of ε-x̄ curves
ε = V̄/πx̄
x̄ = x/a
1.050
1.000
.950
.900
.850
.800
.750
.700
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
4.0
3.0
2.4
2.2
2.1
h̄ = 2.0
h̄ = 1.9
h̄ = 1.8
h̄ = 1.7
h̄ = 1.6
h̄ = 1.5
h̄ = 1.4
h̄ = 1.3
h̄ = 1.2
h̄ = 1.1
h̄ = 1.0

FIG. 3

The theory of the hanging drop has received some experimental confirmation. Gross[1] found that if the head of the liquid above the tip (which we call $\bar{h}-\bar{y}$) is kept constant there is only one stable drop as measured by its length which can hang on a given tip. If, by using suction or pressure, a drop of another size is formed, on restoration of the original pressure the drop will either change to the stable form or else grow until it becomes unstable and detaches. There is another critical length, however. A drop somewhat shorter than this contracts until the stable form is reached; a drop somewhat longer grows until it detaches. The explanation on the basis of the theory of the hanging drop is as follows. Fig. 4 shows the drop profile curves intersected by another series of curves such that each connects points of constant $\bar{h}-\bar{y}$. The independent variables of Gross are our values of $\bar{h}-\bar{y}$ and $\bar{x}$. From the figure it will be seen that the choice of these two variables in general determines two points, that is, two drops. A drop shorter than the smaller is in equilibrium with a pressure $(\bar{h}-\bar{y})$ less than that initially set by the experimenter. When the initial pressure is reestablished, by removing the external pressure or suction, the drop will grow until it is in equilibrium in obedience to the law that liquids run from regions of higher to those of lower pressure. Similarly, a drop somewhat longer than the stable one, having a higher pressure than that due to the head of liquid, will contract until equilibrium is reached. The larger drop determined by the above choice of $\bar{h}-\bar{y}$ and $\bar{x}$ is of another character. A shorter drop than this has a higher pressure; liquid will therefore run out of it until the stable drop is reached. A longer

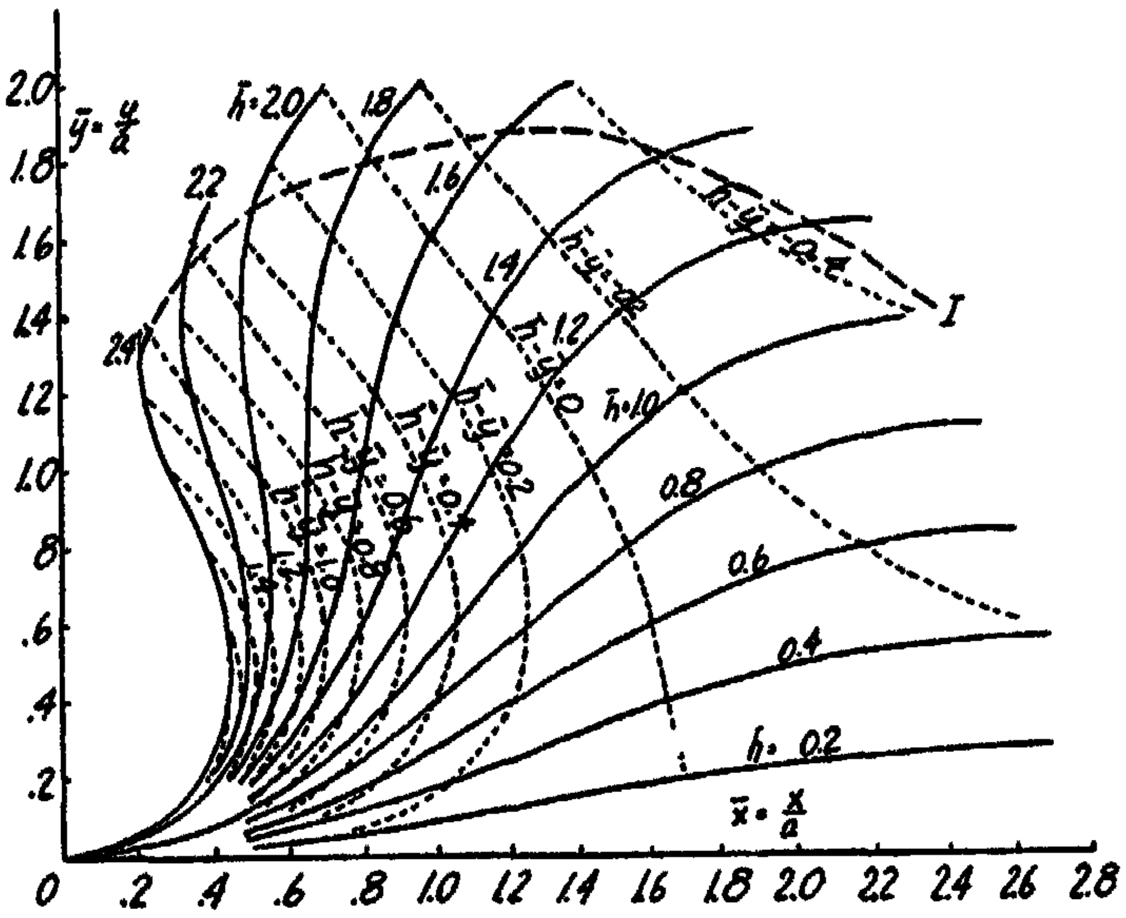

Fig. 4

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[1] P. L. Gross: University of Chicago Dissertation (1926).

drop has a smaller pressure than that due to the head; liquid will run into it continuously until the curve of maximum volume is reached and the drop detaches (see Fig. 4a).

Gross has made a number of experimental observations connecting $\bar{x}$, $\bar{h}-\bar{y}$, and the length $\bar{y}$ of the drop, which on the whole agree with this theory.

The portions of the curves above the curve of maximum volume are unexplained as yet. Possibly they have no physical reality. Thus a drop might assume such shapes if r/a were variable—say when falling from a very large surface. The parts of the curves below the curve of maximum volume are, however, the shapes of the drops before the limiting increment of volume has been added to them which makes them unstable.

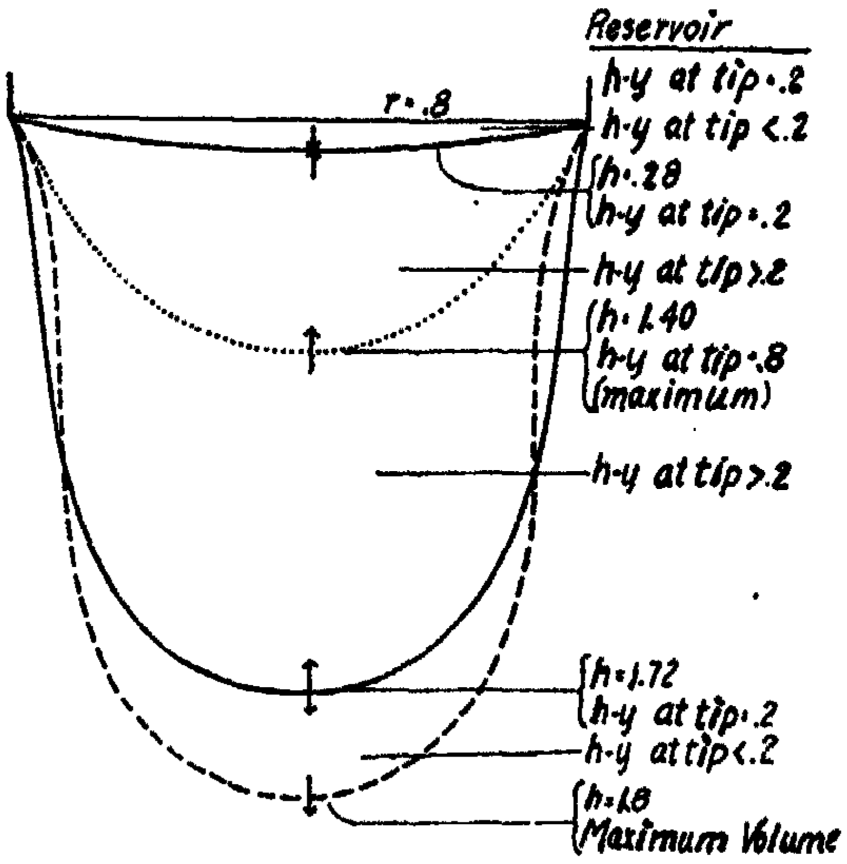

FIG. 4a
Vertical arrows indicate motion of liquid.

The figures discussed above are also interesting in connection with the consideration of the ideal drop. The weight ($W = Mg$) of liquid supported in a capillary tube by surface tension is equal to $2\pi r\gamma$, provided the angle of contact is zero. The maximum weight of liquid supported by a drop weight tip of infinitesimal radius appears to be given by just the same expression. More exactly the value of r/a, not that of r alone, should be very small. The maximum drop which is stable on such a tip is designated by Harkins and Brown[1] as the ideal drop. This use of the term ideal is analogous in a certain sense to its application to gases or solutions, for which ideal behaviour is postulated at infinitesimal concentration. The general theory of the drop indicates that the weight of the ideal drop is that given above, or

$$W = Mg = 2\pi r\gamma \text{ (for the ideal drop).}$$

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[1] Harkins and Brown: loc. cit.

This is supposed to be not only the weight of the maximum hanging drop, but it is very nearly the weight of that which falls, since practically all of the hanging drop detaches.

The above paragraph is entirely in agreement with the theory of Lohnstein, but several writers during the last fifteen years have claimed that the weight of the ideal drop is not $2\pi r\gamma$ but only half of this, or $\pi r\gamma$. The origin of this idea is to be found in the fact that in 1881 Worthington obtained the latter value as the weight of a drop which has "vertical contact" with the tip. That is, the top of the drop was supposed by him to be a cylindrical extension of the vertical outside wall of the tip. His equation for the weight of the maximum drop under such conditions is

$$W = 2\pi r\gamma - \pi r'\gamma = \pi r\gamma$$

in which r is the radius of the tip and r′ that of the curvature of the drop in the plane of the tip. Since these are of necessity equal the equation may seem at first sight to be justified. However a reference to the equations used by Worthington himself a few pages earlier, shows that it is entirely incorrect, since it neglects the curvature in the vertical plane of the surface of the drop at the point of contact. Assuming that the connection of drop with tip is at the narrowest part of the neck, which is probably exactly true only in the limit, the correct equation is, obviously,

$$W = 2\pi r\gamma - \pi r^2\gamma(1/r + 1/s) \tag{5}$$

in which s is this second curvature.

The contour of the smallest drop represented in Fig. 1 shows that at the point of contact with the tip (Curve I) the curvature s has the opposite sign from r, and is numerically almost equal to it. Further, visual observation of drops for much smaller values of r/a indicates the same relation. If r and s are numerically equal the second term of Equation (5) disappears, so

$$W = 2\pi r\gamma$$

which is the weight of this ideal drop as given by Harkins and Brown.

While it is impossible to determine the weight of a drop which falls from an infinitesimal tip, recourse may be made to the same process used with a gas or a solution, extrapolation to a zero value. If the general equation

$$W = 2\pi r\gamma \cdot F$$

is used, it is found that an experimental determination of F gives a value of 0.6 at $r/a = 1$. At low values of r/a as high as 0.93 has been obtained, and the curve extrapolates toward unity. Furthermore the theoretical curve calculated by Lohnstein gives $F = 1$ for $r/a = 0$, and it is seen that the envelope of the curves of Fig. 3 approaches $F = 1$ rather than that of 0.5 as demanded by the equation of Worthington. The theory and the experiments show plainly that it is impossible for a stable hanging drop to have a section at its top which is merely a cylindrical extension of the tip. Unfortunately some recent writers have selected the only incorrect equation of Worthington's excellent paper as its single important contribution to the subject.

The Detached Drop

It is the weight of the completely detached drop which is the easily measurable quantity. It seems reasonable that its weight should be a function of the shape of the stable drop. Nevertheless, the theory connecting the two has not been formulated in any but the crudest manner. An expression, sometimes ascribed to Tate, W = $2\pi r\gamma$, is one of the earliest guesses, although Tate[1] himself did not state his law in this way, but said instead that the weight of the drop is proportional to the diameter of the tip, and also in proportion to the weight of the liquid which would be raised in that tube by

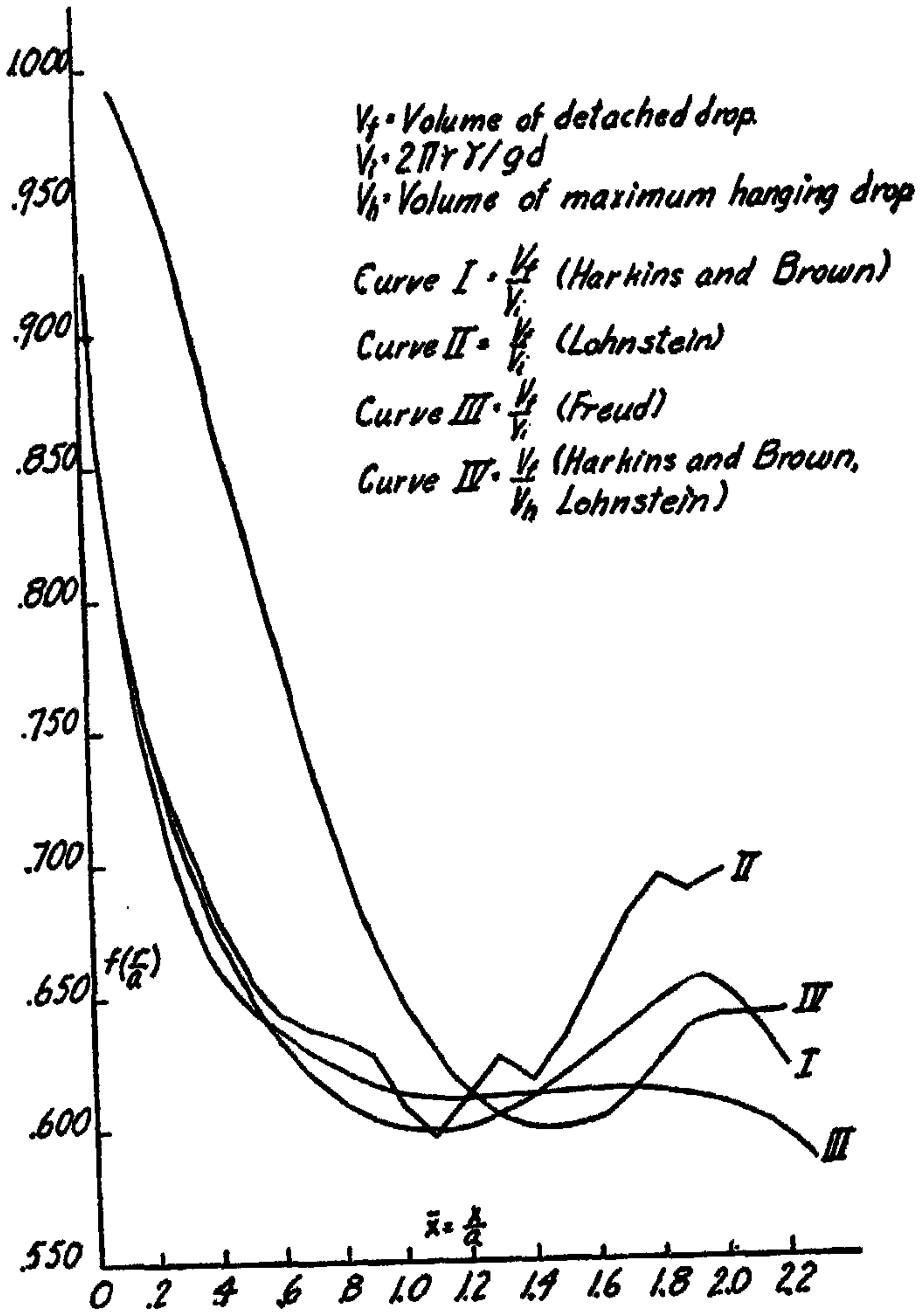

FIG. 5

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[1] Tate: Phil. Mag. (4), 27, 176 (1864).

capillary action. He did not evaluate the proportionality constant. Morgan and Stevenson[1] found that the constant is, for a limited range of r/a, about 0.625. Even in this short range this relationship does not hold exactly. Such relationships are of course empirical, and are not in close agreement with the facts for all values of r/a. Several authors have said that the weight of the detached drop is equal to $2\pi r\gamma$ multiplied by an unknown function of r/a, or the equivalent. Lohnstein evaluates the function, basing his argument on the idea that the portion of the maximum stable drop left on the tip makes the same angle with the tip that the maximum stable drop does. This guess agrees surprisingly well with the facts, although it is possible to construct other relationships which agree as well or better. Thus it might be assumed that the drop breaks in such a way that the length of the profile between the curve of maximum volume and the point of inflection is bisected. This is as unsupported theoretically as the theory of Lohnstein, and has about the same degree of correspondence with the facts, as may be seen from Fig. 5. By appropriate manipulation this could be made to fit the facts much more exactly. No theory has yet been formulated which is at all adequate. Approaching the question from the opposite view point Harkins and Brown have determined an empirical curve which may be used for all liquids, because of the principle that if two drops of two different liquids hang on tips for which the values of r/a are equal, and have also one other dimension, such as the lengths, in the same ratio as the tip radii, they are similar in every other respect, i.e., the profile of one is merely a magnification of the other. This is sometimes called the principle of similitude, and is only the statement in words of the principle stated mathematically in the beginning of this paper when we eliminated "a" from the equation for liquid surfaces of revolution. The drop weight determination carries it a step farther when it is implicitly assumed not only that the shapes of two similar drops are alike, but that the same fraction detaches. This may not be true if the liquid is viscous.

The relation between the weight of the detached drop and any of the constants of the liquid or tip, or even any of the dimensions of the drop just before falling, is therefore far from simple. It seems that the only hope of finding the connection lies in taking the maximum stable drop and in some way following all the changes that take place on detachment.

The Detaching Drop

There is a scarcity of information about the detaching drop in the literature. It consists mostly in photographs of drops taken at varying intervals and rates of fall. Boys[2] gives the profiles of drops of colored water falling into a mixture of paraffin oil and carbon disulfide, taken at intervals of about 1/20 second, in the form of a thaumatrope, but the outlines are not at all

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[1] Morgan and Stevenson: J. Am. Chem. Soc., 30, 360 (1908).

[2] Boys: "Soap Bubbles and the Forces which mold Them" (1896).

distinct. Guye and Perrot[1] have presented a few photographs much like Boys'. Those of Ollivier[2] are not distinct because the drops are too small and are evidently falling very rapidly. Lenard[3] has pictures of a drop at the moment of detaching and at short intervals thereafter. One of these is extremely interesting as the drop profile seems to be angular. This is very similar to one of ours (Figs. 10 and 6c). Our photographs are motion pictures of saturated aqueous solutions of potassium permanganate falling into a solution of stanolin and carbon tetrachloride. The drops show no signs of sharp breaks until the necks are very thin. This fact is not easy to observe when the neck is small, for the change in shape of the drop near the neck is so rapid that even very short exposure of the film gives a negative in which the outline in this region is not distinct. But the pictures do show that the liquid is sufficiently mobile to prevent sharp breaks. The bottom part of the drop pulls away from the tip with an accompanying narrowing and lengthening of the neck. The profiles are perfectly smooth curves. In the very short interval just before rupture, however, the neck becomes very elongated and probably indentations appear which cause the angular appearance of the drop profiles in the photographs. This effect is much plainer in our second series of pictures. These were taken with a super-speed motion picture camera taking 128 frames per second, and the drop was detaching much more rapidly than in the previous series. The long neck and the angular appearance at the joining of the drop and neck are very plain. The later pictures show the way in which the neck divides into small droplets, looking like a pendant of graduated beads. When the drop is falling very slowly the secondary drops are so small as to be almost invisible.

The fundamental difference between the stable and unstable drops lies in the fact that the various parts of the liquid have acquired downward motions. The problem is to formulate them, which at present we see no way of doing. The weight held up by the surface tension is no longer Mg but M(g-G) where G may be considered as analogous to an acceleration. G is a variable and a function of x and y, that is, of the position of the particle in the drop. The factor a^2 in the equation

$$V = \pi x u a^2 - \pi x^2 (h-y)$$

is then no longer constant (we shall call the variable a^2, A^2) and must be so treated in the differentiation, giving

$$\frac{du}{dx} + \frac{u}{x} = -\frac{u}{A^2}\frac{dA^2}{dx} + \frac{2(h-y)}{A^2} \tag{6}$$

When A^2 is constant this reduces to the ordinary static form. We know nothing about the form of the function A^2 except that it must be such that when $x = 0$ and $u = 1$, h and y having any finite value, the conditions for a

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[1] Guye and Perrot: Arch. Sci. Phys. Nat., (4) **11**, 345 (1901); Compt. rend., **135**, 621 (1902).

[2] Ollivier: Ann. Chim., (8) **10**, 229 (1907).

[3] Lenard: Wied. Ann., **30**, 209 (1887).

neck whose sides just touch, the right side of (6) must be equal to infinity. This does not of course take into consideration the secondary drop formation and so would be merely a first approximation. The simplest assumption that satisfies these requirements, that $A^2 = k/x + a^2$, does not prove to be the desired relation, which is of course not at all surprising.

The theory of the detaching drop has thus been barely touched, and much work must be done upon it before the desired relationship can be found.

Summary

1. In this paper the drop weight method is discussed under the three divisions; a.) the hanging drop, b.) the detached drop, and c.) the detaching drop. The theory of the first has been fairly well worked out, the information regarding the second is entirely empirical and there is almost no information or even speculation regarding the third.

2. As a preliminary to the study of the hanging drop many tedious calculations have been made and these are represented by the accompanying figures.

3. Profiles of hanging and detaching drops taken by motion picture cameras are reproduced.

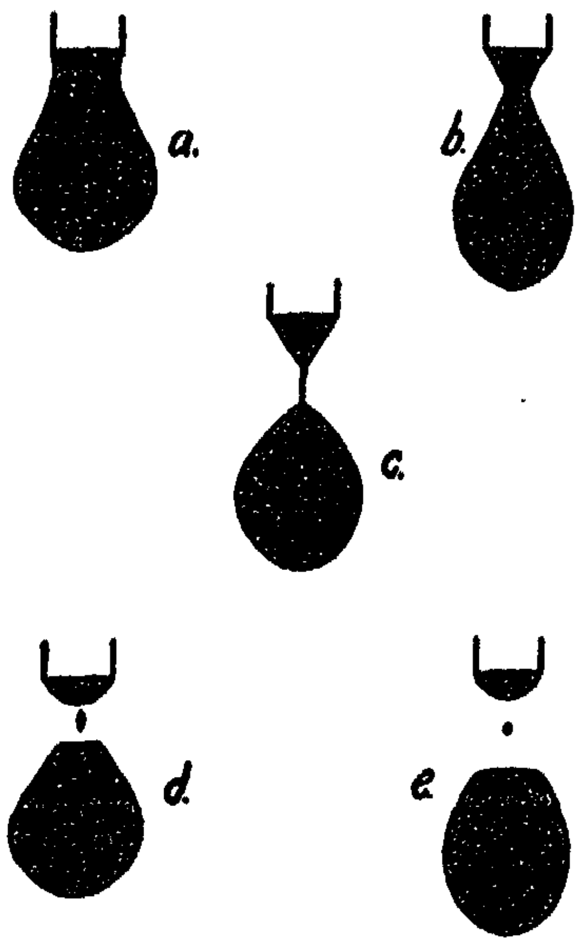

Fig. 6
Shapes of Detaching Drops.
Drawn from Figs. 8-11.

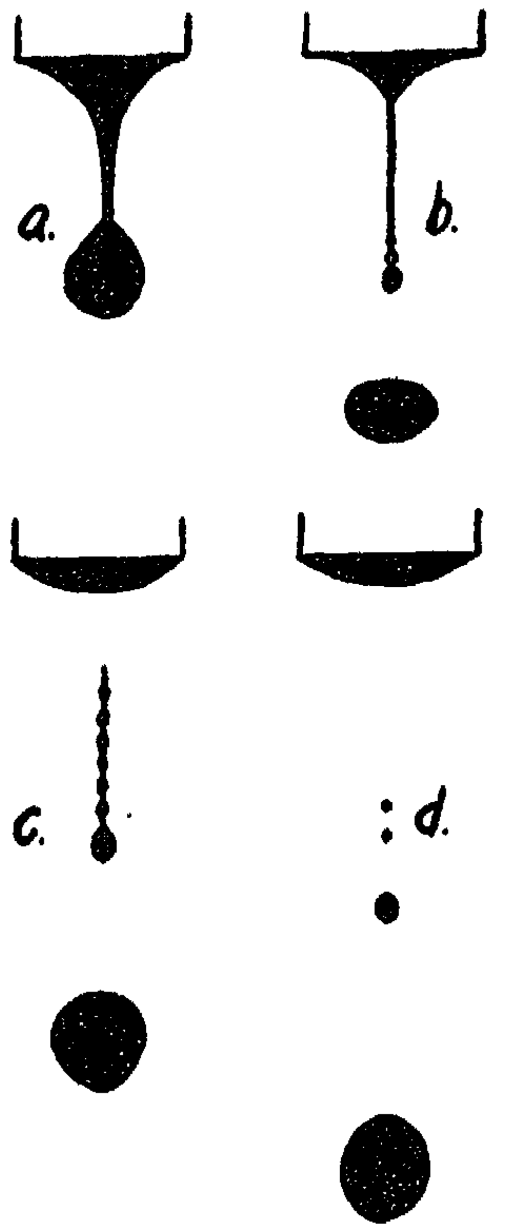

Fig. 7
Rapidly Detaching Drops.
Drawn from Fig. 12.

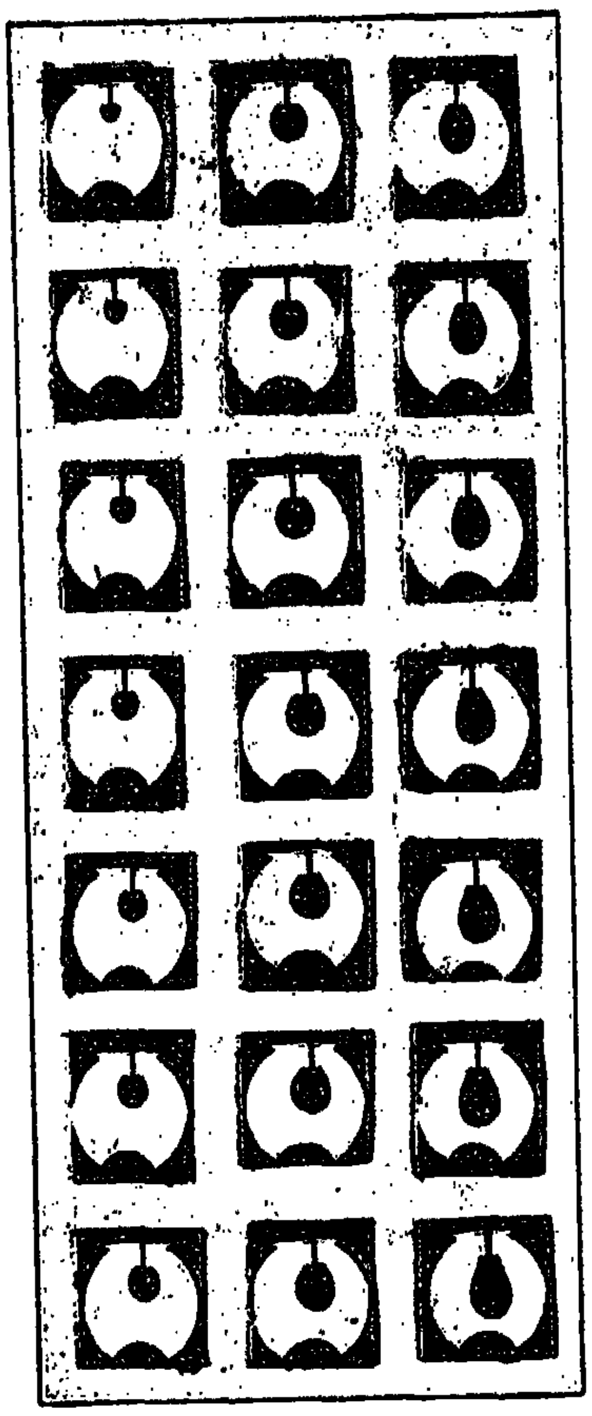

FIG. 8

Profiles of stable hanging drops.
Interval, 6 seconds. Tip, .897 cm.

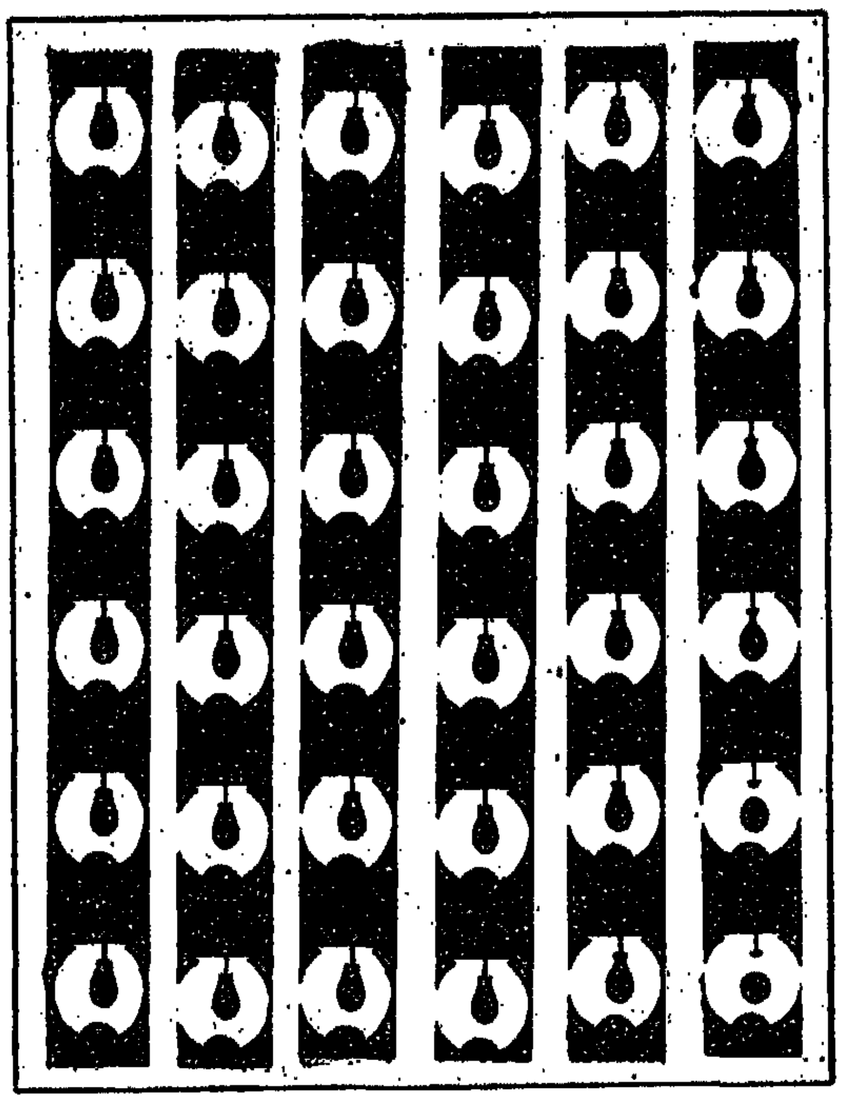

FIG. 9
Photographs of detaching drop.
Interval 1/16 second. Tip .897 cm.
Secondary drop in act of forming.

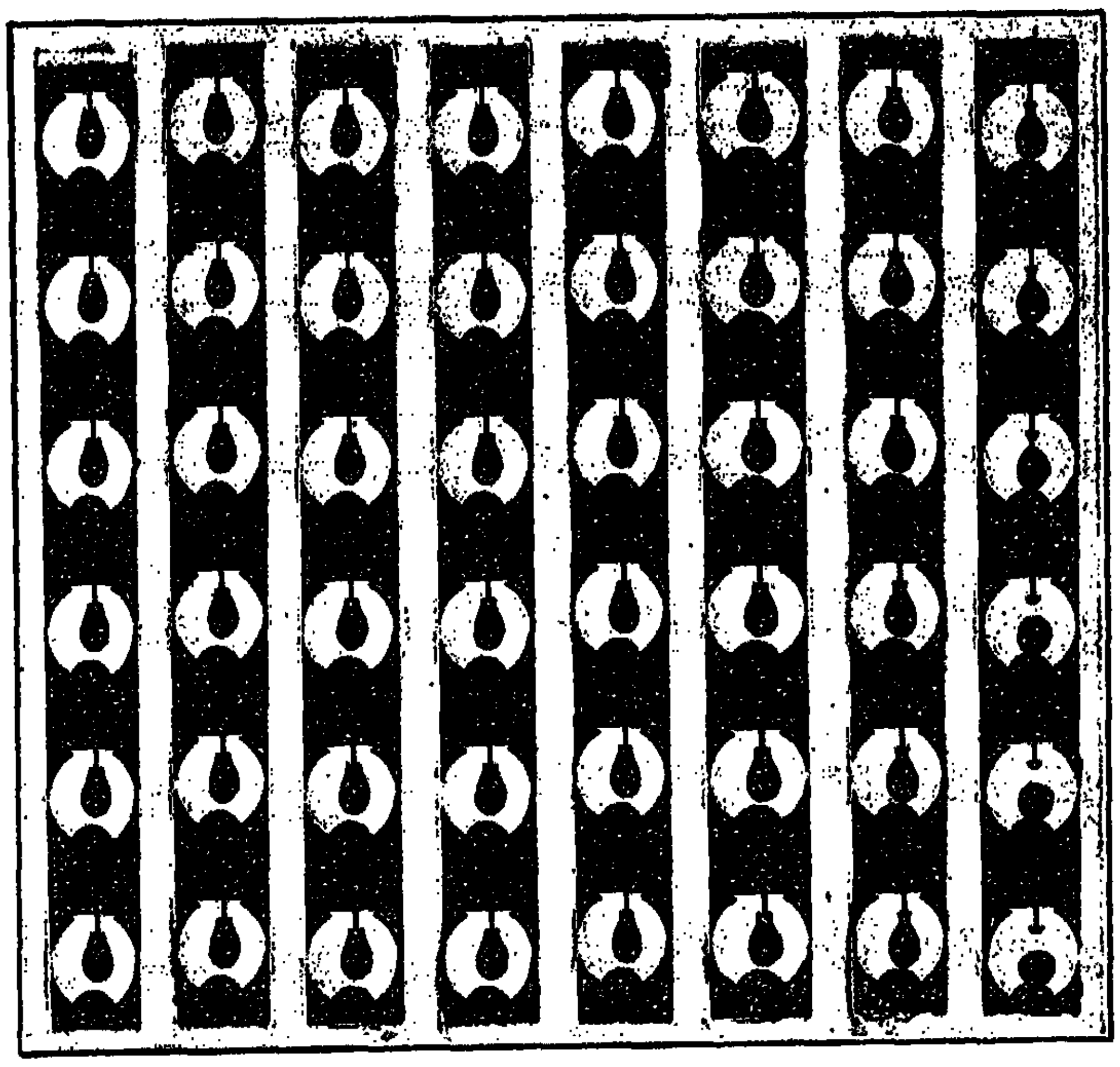

Fig. 10

Photographs of detaching drop. Interval 1/16 second. Tip .897 cm. Showing funnel shape of neck and secondary drop.

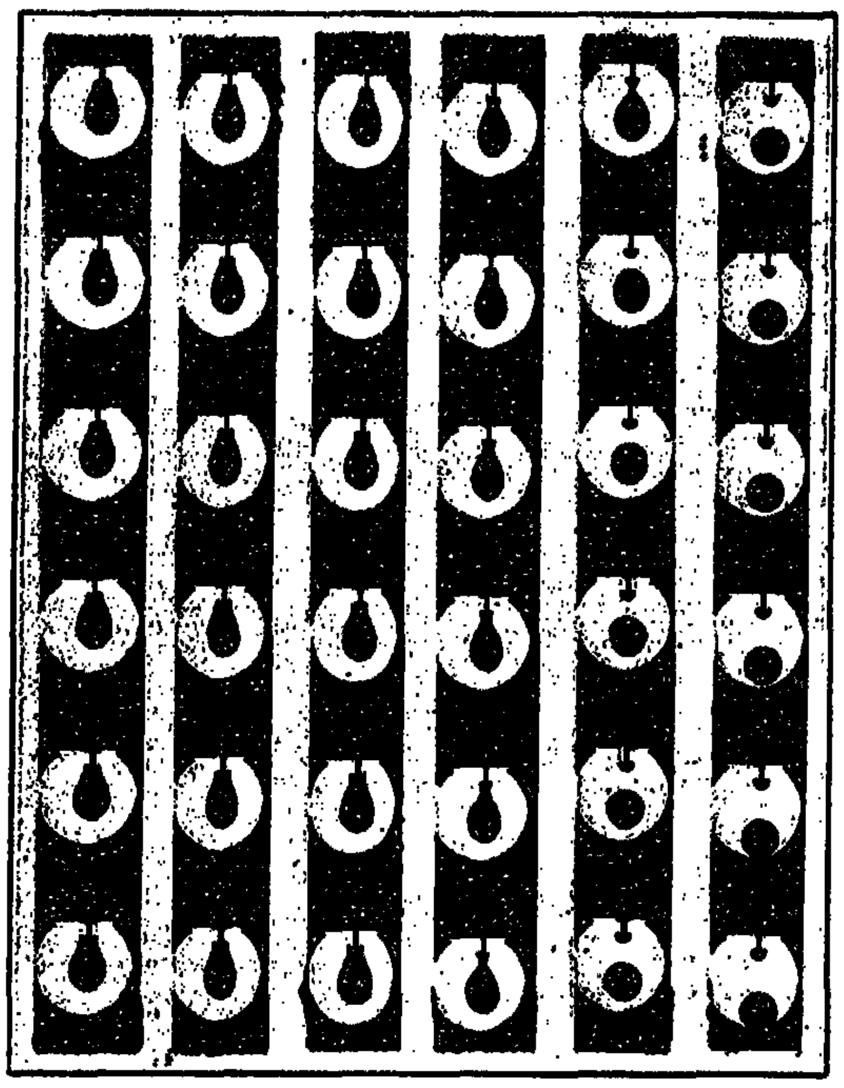

Fig. 11
Photographs of detaching drop.
Showing shape of detached drop.

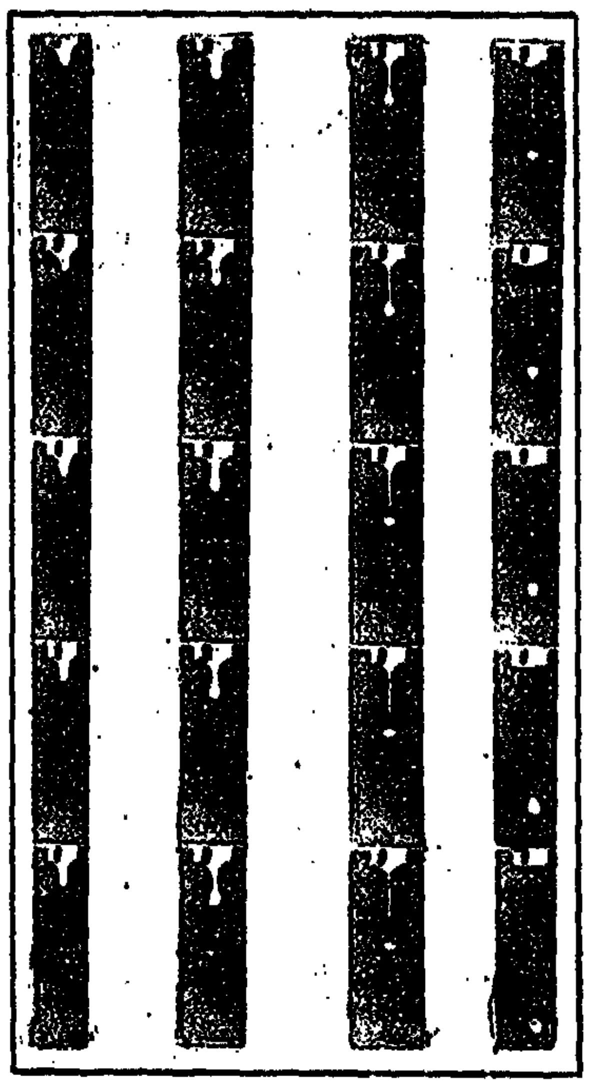

FIG. 12
Photographs of rapidly detaching drop.
Interval 1/128 second.
Tip 1.49 cm. Large r/a. Water detaching into air. Showing beaded secondary drop which divides into several.

STUDIES ON HYDRAZINE: SOLUBILITY RELATIONS OF HYDRAZINE PICRATE, AND THE EQUILIBRIUM $N_2H_5^+ + NH_3 \rightleftarrows NH_4^+ + N_2H_4$*

BY E. C. GILBERT**

Hydrazine forms two complete series of salts in one of which it functions as the ion $N_2H_6^{++}$ and in the other $N_2H_5^+$. By the extended theory of acids and bases[1] these ions may be considered as acids dissociating to give hydrazine and hydrogen ion.

$$(1)\quad N_2H_6^{++} \rightleftarrows N_2H_5^+ + H^+$$

$$(2)\quad N_2H_5^+ \rightleftarrows N_2H_4 + H^+$$

The dissociation constant for reaction (1) has never been measured, though the lower limit for it has been determined by us by the potentiometric method.[2] The exact determination would be a matter of considerable difficulty. The reactions of the salts of this series in solution give no indication of the presence of the divalent ion and they are generally considered as being completely dissociated to give the monovalent ion and hydrogen ion[3].

The dissociation constant for reaction (2) has been determined by Bredig and by Hughes.[4] The results of Bredig are discordant varying from 2.3×10^{-9} to 5.0×10^{-9} with a mean of 4.4×10^{-9} over a range of M/8 to M/256, due to errors inherent in the procedure followed. The more recent value was obtained by Hughes using Haber's glass electrode for a concentration of M/10 and varies from 5.9×10^{-9} to 7.1×10^{-9} depending upon the method of calculation. A dissociation constant for an acid or base is strictly valid only at a particular ionic strength as the constant is dependent upon that quantity,[5] though for a dissociation of this type where the base is an uncharged molecule the effect should be small.

The agreement between the two methods is not good but it indicates that hydrazine as a base is about ten times as weak as ammonia, or conversely hydrazinium ion $N_2H_5^+$ is a ten-fold stronger acid than ammonium ion. A direct comparison of the two might be made by the study of the equilibrium

$$N_2H_5^+ + NH_3 \rightleftarrows N_2H_4 + NH_4^+$$

The constant for ammonia being quite accurately known, that of hydrazine may then be calculated. A direct and simple method of attack would be to

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* Contribution from the Laboratory of Physical Chemistry of the Polytechnic Institute, Copenhagen.

** Fellow of the John Simon Guggenheim Memorial Foundation.

[1] Brönsted: Rec. Trav. chim., **42**, 718 (1923); J. Phys. Chem., **30**, 777 (1926).

[2] Gilbert : J. Am. Chem. Soc., **46**, 2648 (1924).

[3] Bach: Z. physik. Chem., **9**, 241 (1892); Wieland: "Die Hydrazine," 11 (1913).

[4] Bredig: Z. physik Chem., **13**, 308 (1891); Hughes: J. Chem. Soc., **130**, 491 (1928).

[5] Brönsted: Chem. Rev., **5**, 281 (1928); Brönsted and King: J. Am. Chem. Soc., **47**, 2523 (1925).

measure the increase in solubility of a slightly soluble hydrazine salt when a known amount of ammonia is added to the solvent. While the activity of dissolved solutes is a constant so long as they are in equilibrium with excess of the solid the solubility and activity coefficients are very much affected by the total ionic strength of the solvent hence the solvent should consist of a salt solution of sufficient ionic strength to render the effect of the additional salt dissolved in the presence of ammonia unimportant from that standpoint. One complication is the extreme sensitiveness of hydrazine to oxidation in alkaline solution with accompanying formation of hydrogen peroxide which interferes with the customary methods of analysis.[1] This may be avoided by careful deoxygenation of all solutions with a stream of nitrogen. A second complication was the fact that of all the hydrazine salts including both series, none save hydrazine sulfate had been recorded in the literature as being slightly soluble. The sulfate is much too soluble for our use but a series of tests showed the picrate to be relatively insoluble and therefore suited to the purpose. It has the added advantage that picric acid like perchloric forms readily and directly by neutralization the monovalent salt, $N_2H_5.OC_6H_2(NO_2)_3$.

Using this salt a series of determinations was made with water, salt solutions, and ammoniacal solutions as solvent to determine the solubility and equilibrium relations. In the course of the work certain interesting observations were made concerning the behaviour of picrates in homoionic solvents which required data on salts other than hydrazine picrate. These are included in the tables and discussion which follow.

Experimental Part

Preparation of materials. Hydrazine picrate.—Sodium picrate (0.1 mol) was dissolved in hot water and a hot solution of hydrazine monohydrochloride (0.1 mol) was added. Upon cooling, hydrazine picrate separated out as a mass of fine yellow needles. It was collected on a suction filter, washed, and recrystallized from water and alcohol successively. Prepared in a similar manner by Rothenburg[2] in alcoholic solution it had a melting point of 186°C. and analyzed to be the anhydrous salt. Our preparation had a melting point of 201°3. (uncorr.) and titration of the hydrazine indicated the presence of one-half molecule of water of crystallization even after repeated crystallization from alcohol. A weighed sample was dried over sulfuric acid in vacuo and showed no loss in weight, but when heated in an oven at 110° for a half hour it lost weight corresponding closely to one-half molecule of water. Absolute agreement cannot be obtained in this manner as the salt itself will sublime slowly. The loss is very slow after the first half hour, however. Titration of the oven-dried sample for hydrazine showed it to be now 99.2% of the theoretical requirement for the anhydrous salt.

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[1] Gilbert: J. Am. Chem. Soc., in publication.

[2] Rothenburg: Ber., 27, 690 (1894).

Analysis: (a) 0.1 gram of salt was dissolved in water. 25.05 cc. aliquots required 7.37 cc., 7.36 and 7.40 cc. 0.05 N iodic acid to oxidize the hydrazine. Required for $N_2H_5.C_6H_2N_3O_7$; 7.65 cc.; for $N_2H_5.C_6H_2N_3O_7.\frac{1}{2}H_2O$;7.41 cc.

(b) 0.1313 g. heated at 110°C. for one-half hour.

Loss required for one-half molecule of water, 0.0044 g;

Loss found, 0.0043 g.

An attempt was made to titrate the picrate with soidum hydroxide using thymolphthalein (pH 9.0–10.6) as indicator but the color of the solution masked the blue of the endpoint sufficiently to render the method of no value except to furnish additional confirmation that the salt contained one equivalent of picrate to one of hydrazine, rather than two.

Sodium picrate. This was prepared by mixing equivalent proportions of sodium hydroxide and picric acid, Kahlbaum "zur Analyse," in hot solution. The salt was collected on a filter, washed with water, recrystallized from water, washed with alcohol and dried. It contained one molecule of water of crystallization.

Ammonium Chloride. Kahlbaum's best product was recrystallized from water, washed, and dried in air and then at 110°.

Sodium chloride and nitrate. Kahlbaum salts "zur Analyse" were dried and used without further purification.

Triethylamine picrate. A small amount of this material, already prepared, was all that was available.

Tripropylamine picrate. This was prepared from Kahlbaum acid and tripropylamine, and recrystallized from alcohol and water.

Two cobaltammines, *flavo-tetrarhodano-diammine chromiate* and *nitro-rhodano-tetrammine cobaltipicrate* were taken from supplies made previously in this laboratory.

Silver bromate. Made by metathesis from the purest obtainable materials.

Procedure

Solutions. Solutions of the salts were made up by dilution of stronger stock solutions. Flasks and pipettes were calibrated. The ammoniacal solutions were carefully de-oxygenated with a stream of pure nitrogen and the amount of base determined by titration with standard acid. The total ammonia content was checked by distillation of the ammonia into a measured excess of standard acid.

Analysis. Hydrazine was determined by the iodic acid method of Bray and Cuy,[1] using a solution 0.05 N (as oxidizing agent) in iodic acid. The method involves the oxidation of hydrazine by excess iodic acid and back titration with thiosulfate after addition of potassium iodide. It is advantageous because ammonia or picric acid does not interfere and the oxidation equivalent of hydrazine is four giving good accuracy. Tests were made as follows to determine the possible effect of ammonia or picric acid.

(a) Titration of hydrazine in the presence of picric acid.

(1) To 10.02 cc. hydrazine solution (no picric acid present) was added 25.05 cc. iodic acid. 11.52 cc. thiosulfate was required for the back titration.

(2) To 10.02 cc. hydrazine solution (and 1 gram picric acid) was added 25.05 cc. iodic acid. Again 11.52 cc. thiosulfate was required. The test was repeated with no evidence of any interference by the picric acid. The color of the picrate does not interfere with the blue of the starch-iodine endpoint.

(b) Titration of hydrazine in the presence of ammonium picrate.

(1)	Hydrazine Sol'n	Iodic acid	Thiosulfate	Ammon. Pic.
	10.02 cc.	25.05	11.53	0.0
(2)	10.02	25.05	11.52	0.2g.
	"	"	11.53	"

The latter test also confirmed the results of Bray and Cuy who found no interference by ammonia.

The concentration of the cobaltammines and the amine picrates was determined by distilling off the ammonia or amine into excess of standard acid. Here again precautions were observed to ensure that all the base had been driven off and that no decomposition of the picric acid took place. If the solution becomes too concentrated or too alkaline or if solid sodium picrate is formed on the sides of the flask and becomes overheated decomposition takes place and volatile bases are formed.

Solubilities. The slightly soluble salts as prepared above were rotated with water to constant solubility at 20°C. ±0.01. They were then dried somewhat, placed in the appropriate solvent and the process repeated until succeeding samples gave concordant results, the solvent liquid being completely renewed each time.

The solubility bottles and tubes were flushed out with nitrogen carefully before any alkaline solution was introduced into the presence of hydrazine salts. No trace of peroxide was ever detected except in one case where this precaution was omitted. This result was discarded.

Calculations and Discussions

A determination of the solubility of hydrazine picrate in ammonium chloride solutions at 20°C. showed normal behavior, the solubility being expressed up to an ionic strength of 0.12 (measurements were carried no further) by the equation[1]

$$\log \frac{s}{s_0} = 0.5\sqrt{\mu} - 0.25\,\mu$$

Data are given in Table I and Fig. 1.

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[1] Brönsted and LaMer: J. Am. Chem. Soc., **46**, 555 (1924).

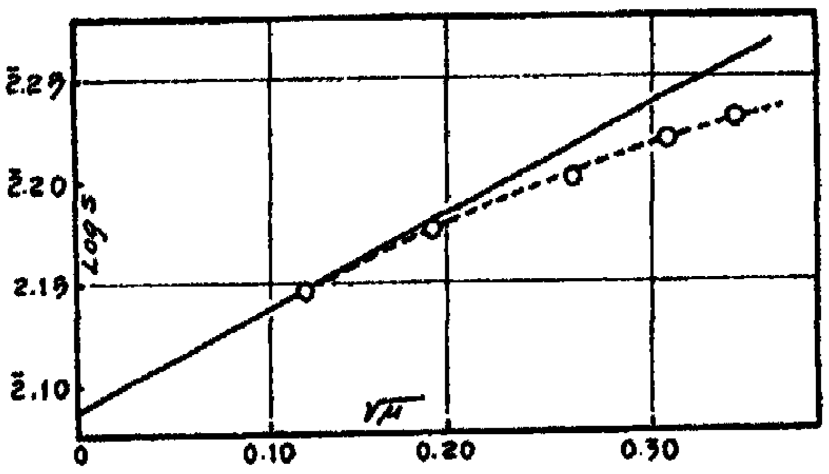

Fig. 1

Solubility of Hydrazine Picrate in NH_4Cl solutions.
Solid Curve = Theoretical for Log $S/S_0 = 0.5\sqrt{\mu}$
Dotted Curve = Experimental Log $S/S_0 = 0.5\sqrt{\mu} - 0.25\mu$

Table I

Solubility of Hydrazine Picrate in Salt Solutions at 20°C

Concentration of added salts						Conc. N_2H_4.Pic.	$k_{s.p.}$ × 10^4
NH_4Cl	$NH_4Pic.$	NaPic.	$NaNO_3$	N_2H_5Cl	NaCl		
—	—	—	—	—	—	0.01395 0.01397	1.95
0.020	—	—	—	—	—	0.01497 0.01501	2.25
0.050	—	—	—	—	—	0.05186 0.01586	2.52
0.080	—	—	—	—	—	0.01654 0.01656	2.74
0.100	—	—	—	—	—	0.01689 0.01691 0.01690	2.86
0.090	0.010	—	—	—	—	0.01310 0.01316	3.03 3.05
0.080	0.020	—	—	—	—	0.01186 0.01191	3.81
0.070	0.030	—	—	—	—	0.01108 0.01108	4.55
0.104	0.0050	—	—	—	—	0.01496 0.01498	2.99

TABLE I (Continued)

Solubility of Hydrazine Picrate in Salt Solutions at 20°C

Concentration of added salts						Conc. N_2H_5.Pic.	$k_{s.p.}$ $\times 10^4$.
NH_4Cl	NH_4Pic.	NaPic.	$NaNO_3$	N_2H_5Cl	NaCl		
0.102	0.0030	—	—	—	—	0.01571	2.94
						0.01562	2.91
0.100	0.0120	—	—	—	—	0.01357	3.47
						0.10362	3.49
0.100	0.01745	—	—	—	—	0.01387	
						0.01388	5.47
0.050	0.010	—	—	—	—	0.01210	
						0.01208	2.67
0.100	0.010	—	—	—	—	0.01390	
						0.01386	3.30
0.100	0.0050	—	—	—	—	0.01495	
						0.1495	2.98
—	—	—	0.100	—	—	0.01611	
						0.01610	2.59
—	—	0.100	—	—	—	0.04316	4.49
						0.04329	4.50
0.090	—	—	—	0.009793	—	0.01230	
						0.01233	2.72
0.080	—	—	—	0.01959	—	0.00903	
						0.00904	2.59
0.070	—	—	—	0.02952	—	0.00688	
						0.00691	2.52
At 15°C							
—	—	0.100	—	—	—	0.00314	3.24
—	—	0.0500	—	—	0.0500	0.00413	2.23
—	—	—	—	—	0.100	0.01176	1.38

To determine the constant for the equilibrium

$$N_2H^+_5 + NH_3 \rightleftharpoons NH^+_4 + N_2H_4$$

and thereby the dissociation constant of the $N_2H_5^+$ ion, an amount of ammonia calculated to give a maximum increase of about 20% in the solubility of hydrazine picrate was added to 0.1 M ammonium chloride (oxygen-free) and after determination of the solubility, calculations were made as follows:

(1) The total amount of hydrazine determined by titration is the sum of $N_2H_5^+$ and N_2H_4. It is also equal to the concentration of picrate ion.

(2) The solubility or ion product having been previously determined, ($K_{s.p.}$ picrate ion) gives $N_2H_5^+$. From this and (1) N_2H_4 may be determined by subtraction.

(3) By the procedure used the concentration of N_2H_4 is stoichiometrically equivalent to the ammonia which has reacted, and the equilibrium concentration of ammonia may be obtained from this figure and the original ammonia concentration by subtraction.

(4) The amount of N_2H_4 formed is also equivalent to the amount of ammonium ion formed and the equilibrium concentration of ammonium ion may be obtained by adding ammonium ion formed to the original concentration of the solvent.

(5) The equilibrium constant obtained from these figures can readily be shown to be equal to the ratio of the dissociation constants

$$\frac{k_{N_2H_5^+}}{k_{NH_4^+}} = K_{eq.} = \frac{N_2H_4 \times NH_4^+}{N_2H_5^+ \times NH_3} \qquad (4)$$

The dissociation constant for ammonia has been carefully determined[1] 1.765×10^{-5}.

The dissociation constant of the ammonium ion as an acid is related to this constant for ammonia as a base by the equation

$$K_{Acid} \cdot K_{Base} = K_{H_2O}$$

Using the value of Michaelis[2] 0.9×10^{-14} at 20° for K_{H_2O}, K_{Acid} becomes 5.10×10^{-10}. Substituting this value in equation (4) a value for the dissociation constant of the hydrazinium ion may be derived. Data are given in Table II.

Previous work on another reaction had given strong indication however that the solubility or ion product of hydrazine picrate depends not only upon the ionic strength but also upon the particular ions which may be present. In dilute solutions as a general rule the chief factor in determining solubility and the activity coefficients is the total ionic strength. It is recognized however that there are in addition in many cases specific effects of individual ions.[3]

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[1] Noyes, Kato, and Sosman: Z. physik. Chem., 73, 1 (1910).

[2] Michaelis: "Die Wasserstoffionenkonzentration," (1914).

[3] A. A. Noyes: J. Am. Chem. Soc., 46, 1115 (1924).

TABLE II

Solubility and Equilibrium Data for Hydrazine Picrate in Ammonium Chloride-Ammonia Solutions, 20°C

Orig. Conc. NH_4^+	Orig. Conc. NH_3	Total Picrate	$K_{s.p.} \times 10^4$	Equilibrium concentrations $N_2H_5^+$	N_2H_4	NH_4^+	NH_3	K for equil.	K_A for $N_2H_5^+ \times 10^9$
0.100	0.01230	0.02208	3.16	0.01433	0.00775	0.1077	0.00455	12.80	6.51
0.100	0.01000	0.02091	3.07	0.01467	0.00624	0.1062	0.00376	12.00	6.12
0.100	0.00606	0.01922	2.97	0.01546	0.00376	0.1038	0.00230	10.96	5.58
0.100	0.00289	0.01793	2.89	0.01612	0.00181	0.1016	0.00107	10.70	5.46
0.100	0.01216	0.02193	3.15	0.01436	0.00757	0.1076	0.00457	12.40	6.32
0.100	0.00955	0.02078	3.06	0.01476	0.00602	0.1060	0.00353	12.26	6.25
0.100	0.00640	0.01936	2.97	0.01534	0.00392	0.1039	0.00248	10.70	5.46
0.100	0.00300	0.01796	2.89	0.01609	0.00187	0.1019	0.00113	10.65	5.43
0.0638	0.00588	0.01856	2.69	0.01450	0.00406	0.0677	0.00182	10.45	5.33
0.0563	0.00352	0.01742	2.59	0.01487	0.00255	0.0589	0.00097	10.40	5.31

The individual effect of ions in addition to that of their valence charge seems to be particularly pronounced with picrates. The effect does not become noticeable as long as the solvent salts possess no common ion and hydrazine and picrate are present in equivalent amounts. This is evident in the normal behavior of hydrazine picrate in ammonium chloride solutions, Fig. 1. Further, the effect seems to be due mainly to the picrate ion. The solubility product is not the same by many percent in 0.1M sodium chloride as it is in a solution 0.08M in sodium chloride and 0.02M in sodium picrate. The effect of the picrate is superimposed on the effect of increased ionic strength and the two are somewhat difficult to evaluate separately. The equilibrium of hydrazine and ammonia showed evidence of this phenomenon as the use of a constant solubility product over a range of concentrations gave an enormous drift in the equilibrium constant. Formation of free hydrazine in the reaction results in inequality between the concentration of hydrazinium and picrate ion and the effect comes into prominence.

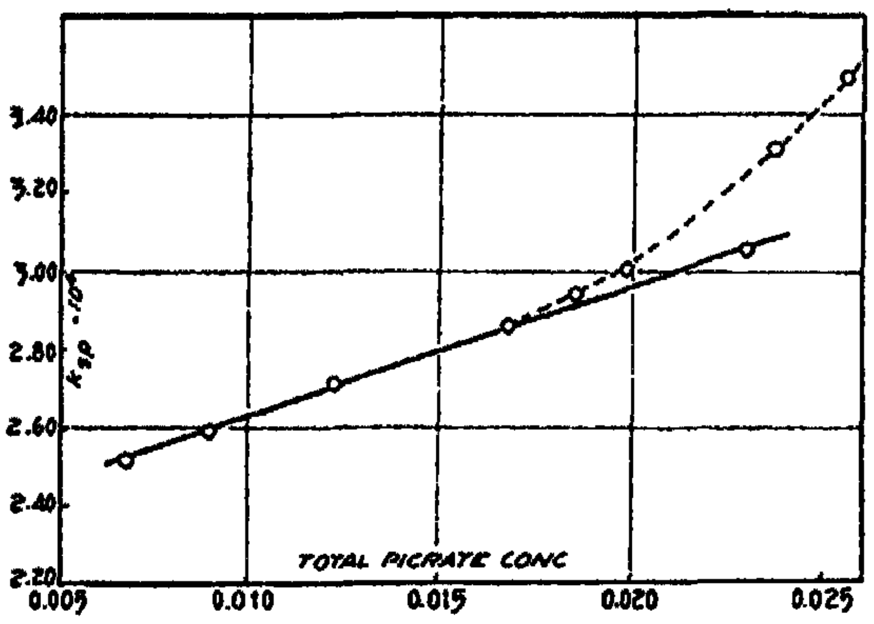

FIG. 2

Change of $k_{s.p.}$ of Hydrazine Picrate in NH_4Cl — NH_4Pic — N_2H_5Cl Mixtures.
Solid Curve Conc. of solvent salt = 0.1M.
Dotted Curve Conc. of solvent salt variable but > 0.1M.

A careful study of the solubility of hydrazine picrate in solutions of ammonium chloride, hydrazine monohydrochloride, and ammonium picrate was made in order to arrive at figures which could be used for the $K_{s.p.}$ in our various equilibrium mixtures. In Fig. 2 the solid line represents the change in solubility product with change in picrate ion concentration, the added salt concentration being maintained at 0.1M. The points to the left were obtained by replacing part of the ammonium chloride by hydrazine hydrochloride, while the higher ones to the right represent substitution in part of ammonium picrate for ammonium chloride. It is essentially a straight line though unavoidable variations in the total ionic strength amounting to a few percent undoubtedly affect the slope. When the added salt is increased above 0.1 M the solubility product increases more rapidly (along the dotted line in Fig. 2). This represents the change in passing from a solution of 0.1 M ammonium chloride to 0.1 M ammonium chloride plus 0.012 M ammonium picrate. Here both the picrate ion and the total ionic strength are increasing rapidly. This dotted line represents also as nearly as possible the proportions of our equilibrium experiments (except the last two in Table II) and from it the solubility products were taken for calculation. A similar procedure not plotted was adopted for the last two.

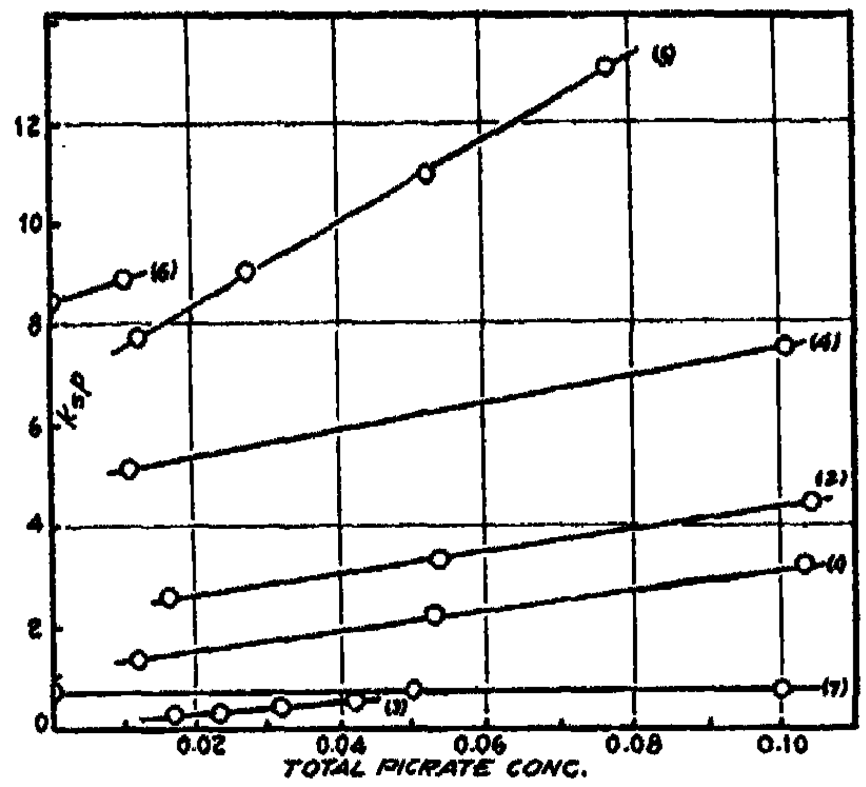

FIG. 3
Effect of Picrate-ion on Solubility Product of slightly Soluble Salts.

Saturizing Salt	Solvent Salts (Total conc. solv. salts = 0.1 M)
(1) Hydrazine Picrate	NaCl Pic 15°C.
(2) " "	$NaNO_3$ – NaPic. 20°C.
(3) " "	NH_4Cl – NH_4Pic.
(4) Tripropyl amine Picrate	NaCl – NaPic.
(5) Dinitrito tetrammine Cobalti Picrate	NaCl – NaPic.
(6) Flavo-tetra rhodano diammine chromiate	NaCl – NaPic.
(7) Silver Bromate	$NaNO_3$ – NaPic.

The question also arose as to whether this phenomenon is peculiar to hydrazine picrate, alone perhaps due to the hydrazine. To answer this the solubility of hydrazine picrate was determined in various salt solutions and then several other slightly soluble salts were also investigated, particularly with respect to their solubility in the presence of picrate ions.

Results, Tables II and IV, and Fig. 3, show this behavior to be quite general with picrate salts. Upon changing from 0.1M ammonium chloride to 0.1 M sodium nitrate as solvent the ion product of hydrazine picrate changes about 8% but in changing to 0.1 M sodium picrate instead we find an increase of 50%. Triethylamine and tripropylamine picrate show the same effect. With the latter there is an increase of ca. 50%. With dinitrito-

TABLE III

Solubilities of Cobaltammine Salts in NaCl-NaPicrate Mixtures

(A) Croceo-Di-Nitro-Tetrammine Cobalti-Picrate

Concentration of added salts		Concentration of saturating salt	$k_{s.p.}$
NaCl	NaPic		
0.100	—	0.008796	
		0.008807	7.75×10^{-6}
0.075	0.025	0.003221	
		0.003225	9.09 "
0.050	0.050	0.002116	
		0.002109	11.0 "
0.025	0.075	0.001702	
		0.001708	13.1 "
—	0.100	0.001516	
		0.001520	15.4 "

(B) Flavo-Tetra-rhodano-Diammine Chromiate

NaCl	NaPic	Concentration of saturating salt	$k_{s.p.}$
0.100	—	0.000917	8.47×10^{-7}
		0.000925	
0.090	0.0100	0.000945	
		0.000945	8.93 "

TABLE IV

Solubilities of Alkylamine Picrates in NaCl-NaPicrate Mixtures

(A) Triethylamine Picrate

Concentration of added salts		Concentration of saturating salt	$k_{s.p.}$
NaCl	NaPic		
0.100	—	0.07730	
		0.07508	5.64×10^{-3}
—	0.100	0.00608	
		0.00598	9.56×10^{-3}

(B) Tripropylamine Picrate

NaCl	NaPic	Concentration of saturating salt	$k_{s.p.}$
—	—	0.00569	3.23×10^{-5}
		0.00569	
0.100	—	0.00720	
		0.00717	5.16 "
—	0.100	0.00075	
		0.00075	7.54 "

TABLE V

Solubility of Silver Bromate in $NaNO_3$-NaPicrate Mixtures

Concentration of added salts		Concentration of	
$NaNO_3$	NaPic	$AgBrO_3$	$k_{s.p.}$
—	0.100	0.00848	7.2×10^{-5}
0.100	—	0.000837 0.00844	7.1 "
0.050	0.50	0.00837 0.00840	7.1 "

tetrammine cobalti-picrate (croceo) the change is nearly 100% in changing from sodium chloride to sodium picrate of the same concentration, (0.1 M).

Finally, two salts not picrates were used. Flavo-tetra-rhodano diammine chromiate showed a large increase in solubility but the available range was small due to the slight solubility of the picrate of this salt. On the other hand silver bromate showed no change in solubility beyond the limits of our experimental error between sodium nitrate and picrate. It seems likely, therefore that the effect is to be anticipated most surely in slightly soluble picrates and allowance must be made for such deviation.

Corrected as well as possible from our data the equilibrium constant between hydrazine and ammonia shows a certain drift with changing concentration, which is reflected in the dissociation constant for the hydrazinium ion Our result however, agrees well with that of previous investigators. It is of course valid only at the concentrations here used.

The author wishes to express his gratitude to the John Simon Guggenheim Memorial Foundation and the Regents of the Oregon State College for providing opportunity for this work and to Professor Brönsted for the hospitality of his laboratory.

Summary

(1) Hydrazine picrate is pointed out as a sparingly soluble hydrazine salt suitable for easy and accurate solubility studies.

(2) The solubility of this and other picrates in salt solutions showed a considerable deviation from the law of constancy of the ion product where the solvents had a common ion. This effect is not noticeable except in homoionic solvents and is apparently a specific effect of the picrate ion.

(3) The constant for the equilibrium between hydrazine and ammonia and their salts has been determined at 20°C.

(4) From this a value of $5.3 - 6.5 \times 10^{-9}$ has been calculated for the dissociation of the ion $N_2H_5^+$. This corresponds to a dissociation constant of hydrazine as a base of 1.4-1.7×10^{-6} in solutions of ionic strength 0.07–0.125.

Copenhagen,
April 8, 1929.

THE COLORS OF COBALTOUS HYDROXIDE

BY CHARLES W. STILLWELL

When an excess of caustic potash is added to a solution of a cobaltous salt a voluminous, deep blue precipitate is formed which later turns to rose cobaltous hydroxide. This change was probably first studied by Winkelblech.[1] He also noted the appearance of green flakes if the precipitation was made in dilute solution. Winkelblech's conclusion is that the blue is a basic salt of cobalt and that the green is the same thing partially oxidized. In 1912 Hantzsch showed[2] that the blue precipitate is also cobaltous hydroxide but that it adsorbs strongly the cobaltous salt from which it is precipitated, or a basic salt of cobalt formed during the precipitation. He postulates hydrate isomers, blue $CoO.H_2O$ and red  $Co(OH)_2$, the former being stabilized by the adsorbed salt. Weiser[3] reviews the pros and cons of the matter, casting aside the explanation of Hantzsch and offering evidence to indicate that the blue may be due to finely divided particles and the red to larger particles; or that we may be dealing with two allotropic forms of cobaltous hydroxide. The present work was undertaken to determine which, if either, of these explanations is the true one.

Many workers have endeavored to explain the change in color of a cobalt solution from red to blue as concentrated acid is added, and it was thought that this controversy might throw light on the present problem. Hantzsch,[4] studying absorption spectra, concludes that in the red solution the cobalt atom is associated with six other groups, while in the blue the cobalt is associated with four. Howell[5] reached the same conclusions independently by a comparison of the absorption spectra of the solutions with the absorption spectra of solids whose crystal structure had been determined by X-ray analysis. More recent papers seem to support this general idea.[6] If these conditions hold for the cobaltous hydroxides we should expect a difference in the crystal structure of the two, and there is further evidence to substantiate this. Small amounts of nickelous hydroxide precipitated with the cobaltous hydroxide will retard the change from blue to rose.[7] This could be explained by assuming that the crystal structure of the blue more closely corresponds to that of the nickelous hydroxide than does the crystal struc-

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[1] Ann., 13, 155 (1835).

[2] Z. anorg. Chem., 73, 304 (1912).

[3] "The Hydrous Oxides," 147.

[4] Z. anorg. Chem., 73, 309 (1912).

[5] Phil. Mag., (6) 48, 833 (1924). This paper contains a complete bibliography of earlier work.

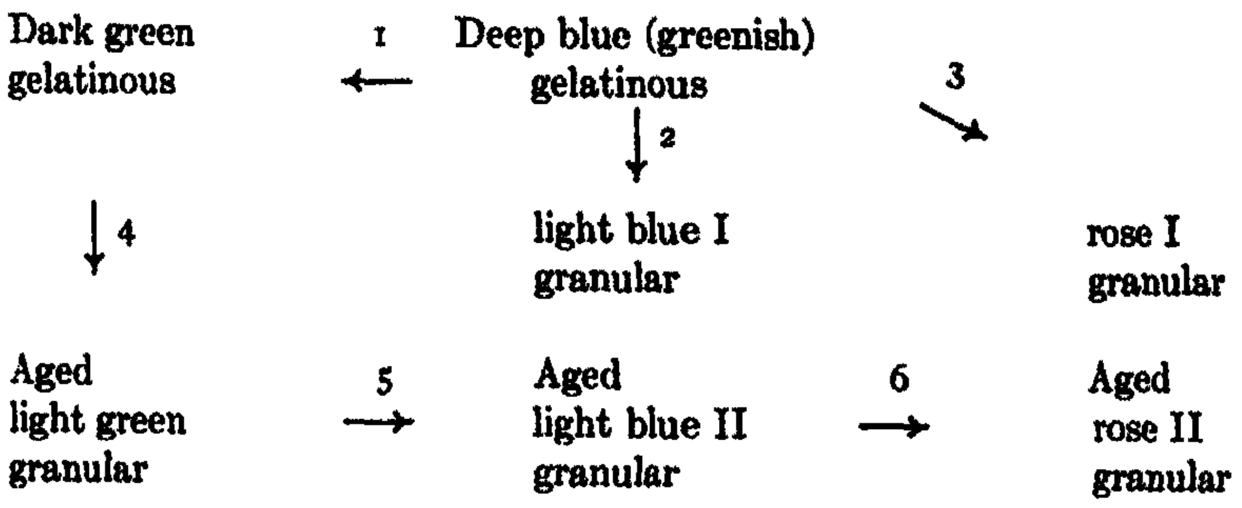
[6] Howell: J. Chem. Soc., 1927, 158, 2039, 2843; Hantzsch: Z. anorg. Chem. 159, 273 (1927): 166, 237 (1927).

[7] Benedict: J. Am. Chem. Soc., 26, 695, (1904); Proc. Indiana Acad. Sci., 34, 163 (1924).

ture of the rose. Several similar cases are known; notably red and green chromic oxide with alumina[1], red and yellow mercuric iodide with mercuric bromide,[2] and yellow and orange silver iodide with silver bromide.[3]

Before investigating the crystal structures of the blue and rose cobaltous hydroxides, the conditions necessary for their preparation were studied in more detail.

When potassium hydroxide is added to cobaltous chloride the first precipitate is always deep blue and gelatinous, laminar in appearance, regardless of the relative proportions of reactants used. If the precipitate subsequently changes to green, it has a noticeable greenish tinge immediately after mixing; that is, although predominately blue it is not as pure a blue as those which subsequently undergo change one or two in the chart below. If concentrated solutions are used, say two molar, a stiff gel is actually formed and later experiments show that the original deep blue color can only be preserved in the stiff gel. As soon as the gel breaks down, aging and a change of color set in. The gel may be stabilized and the deep blue color maintained by adding glycerine, as well as by using more concentrated solutions. Under normal conditions this deep blue may change either to green, or through violet to rose, or may remain blue—a lighter blue—depending upon the relative amounts of reactants used. Under certain conditions the green changes on long standing first to blue and then to rose. The following diagram indicates all these changes:



It is shown below that the blue and rose prepared directly are different from the same colors obtained by the aging of the green precipitate, and the former are therefore separate and are designated "blue I" and "blue II" although superficially the two blues appear identical as do the two roses. The aged precipitate and changes four, five and six are discussed in section II. The immediate discussion deals with changes one, two and three.

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[1] Stillwell: J. Phys. Chem., 30, 1441 (1926).

[2] Mellor: "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," 3, 427.

[3] Mellor: Ibid., 4, 504.

The color changes of the deep-blue precipitate and the rate of change depend on several factors. The deep blue to rose change is accelerated by

1. Heating[1]
2. Increasing the concentration, keeping the molar ratio of reactants constant.
3. Increasing the ratio moles KOH to moles $CoCl_2$, keeping the concentration constant.

This change in color is accompanied by a visible settling of the precipitate and a change from gelatinous laminae to granules.

The deep-blue to green change is accelerated by

1. Decreasing the concentration, keeping the molar ratio constant.
2. Increasing the excess $CoCl_2$ added, keeping the concentration constant.

The green precipitate remains gelatinous and there is no evidence of settling.

The deep-blue to light-blue change depends on the molar ratio of the reactants. The light-blue is a granular precipitate and settles to about half the volume of the original precipitate, occupying about the same volume that an equal weight of rose precipitate would occupy.

The following series of experiments was run in order to determine more accurately the conditions controlling these changes and to explain the part played by the cobaltous chloride in excess. To fixed amounts (10 cc.) of 0.83M $CoCl_2$ varying amounts of 1.55M KOH were added, the resulting precipitate shaken well and small amounts of the mother liquor filtered off and tested for cobalt. The remaining precipitate was allowed to stand in the test tube for several days and the supernatant liquid was again tested for cobalt. The results are given in Table II.

TABLE II

No.	Vol. KOH added	Molar ratio $CoCl_2$:KOH	After five minutes Co test color	After four days Co test color
1	9.0cc	1 : 1.68	+ green	+ green
2	9.4	1 : 1.76	+ bluish-green	+ bluish-green
3	9.5	1 : 1.78	+ greenish-blue	+ bluish-green
4	9.6	1 : 1.80	− blue	+ blue
5	10.0	1 : 1.87	− blue	+ blue
6	10.5	1 : 1.96	− blue	+ reddish-blue
7	10.76	1 : 2	− reddish-blue	− rose

It has already been shown by Hantzsch[2] that the cobalt salt is adsorbed and does not form a basic salt.[3] The results indicate that the cobalt ion is adsorbed in considerable amount. The washed and dried precipitates always evolve hydrogen chloride when treated with concentrated sulfuric acid,

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[1] Winkelblech: Ann., 13, 155 (1835).

[2] Z. anorg. Chem., 73, 304 (1912).

[3] It is shown on p. 1270 that when a greater excess of $CoCl_2$ is used a basic salt is formed, but that does not concern the present discussion.

indicating that chloride is also adsorbed. From the table it is evident that between molar limits 1 $CoCl_2$: 1.8 KOH and 1 $CoCl_2$: 1.95 KOH the blue precipitate remains blue in the test tube indefinitely, changing only from a dark, gelatinous to a light granular form. With more $CoCl_2$ the precipitate turns green on standing, the rate of change depending on the concentration of the excess cobaltous chloride, probably because more cobaltous chloride is actually adsorbed. As the amount of adsorbed cobaltous chloride decreases the tendency to change from blue to rose increases.

Dhar[1] has investigated the effect of adsorption on the color of various precipitates, finding that certain ones are greatly affected. But in the present instance the adsorption is not directly responsible for the color changes because the blue appears for a limited time even when an excess of potassium hydroxide is used. Rather, the cobaltous hydroxide naturally forms first as a gelatinous, laminar precipitate and a moderate amount of adsorbed cobaltous chloride stabilizes this. If insufficient cobaltous chloride is present it will change slowly to the rose, and an excess of cobaltous chloride produces the green. The blue to rose change could not be reversed by allowing rose cobaltous hydroxide to stand three weeks in contact with an excess of cobaltous chloride solution,[2] and this suggests that the change is from a metastable to a stable form. The occurrence of cobalt ion in the supernatant liquid after several days where none was present when fresh, indicates that as crystallization progresses the cobaltous chloride is released. This too shows that the adsorbed salt merely inhibits crystallization and does not take part in it. This was corroborated by the X-ray diffraction pattern for cobaltous hydroxide containing adsorbed salt, since the pattern was not altered by the presence of the cobaltous chloride.

It has been stated that nickelous hydroxide will retard the blue to rose change, when added in small amounts. It was found that if a larger amount of nickelous hydroxide (5%) were added to a precipitate which would normally remain blue, it would turn green. This, coupled with the effect of cobaltous chloride, suggests that the real causal sequence of the color change is green to blue to rose; that since the blue is stabilized by intermediate amounts of either of these substances, its properties must be intermediate. Since the blue and rose precipitates are the same chemically, a difference in physical properties is to be expected, and it was detected by following the color changes microscopically and with X-ray diffraction patterns. It should be emphasized that the actual sequence of color change is never from green to blue. Once conditions have produced the blue to green change, it does not reverse, except under the exceptional conditions discussed in Section II Since the blue to green change has heretofore been attributed to partial oxidation it was necessary to investigate that point before assuming it to be due merely to cobaltous hydroxide with different physical properties.

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[1] J. Phys. Chem., 29, 1394 (1925).

[2] Farnam and Wittween: J. Ind. Eng. Chem., 13, 1060 (1921), claim that under such conditions the rose to blue change does occur, but their experiment could not be duplicated.

The tendency of the freshly-precipitated blue to turn green was mentioned by Winkelblech,[1] but he notes that analysis showed only 0.5% more oxygen in the green than in the blue. This might be sufficient to give a surface film of green, but the precipitate in question is green throughout. Hantzsch noted that the least quantity of air would cause the blue to change to green.[2] Bernardi in a recent paper[3] has called attention to this, stating that the green precipitate is stable only when the ratio of mols of cobalt salt to mols of sodium hydroxide is between 1:0.02 and 1:0.44. He states that in the absence of oxygen only blue precipitates are obtained which turn green when air is bubbled thru them. Of course, there is no doubt but what partial oxidation of the blue would give a green precipitate. Cobaltic hydroxide is brown and a mixture of brown and blue would give green; but the following observations will make it clear that the change occurs as a result of some other cause.

1. Using exactly the same degree of caution to exclude air, one may prepare a green or a blue precipitate simply by varying the ratio of cobalt chloride to potassium hydroxide. The change from blue to green on standing cannot be due to diffusion of air into the mass because it changes uniformly throughout. On the other hand, the blue one will after a couple of days have a brown layer on top and then a green layer beneath. This green is of course due to oxidation.

2. When a blue precipitate is poured on a filter paper and exposed to the air it turns green, the change being faster the greater the excess of cobalt chloride. The green color remains indefinitely. If a little potassium hydroxide is added it reacts with the excess cobalt salt, restoring the blue color. Now on standing, the color changes first to green and then to brown and the blue cannot be restored. Obviously this second change is due to oxidation and shows definitely that the first one is not.

3. A blue precipitate may be prepared, placed in a desiccator to dry and found to have a thin layer of green on the outside with the inside a good blue. This green is due to oxidation. But a lump may be green all thru, or it may be blue when in the lump and turn green instantaneously when powdered. These changes could not be due to oxidation.

4. A blue precipitate formed in the absence of air in dilute solution and using a light excess of cobalt salt is green by transmitted light. A very heavy precipitate, blue, will appear green if held in direct sunlight. In this case the light is sufficiently intense to penetrate the surface particles so we really get the color of transmitted light.

5. Bernardi's experiment in which a change from blue to green occurs when air is bubbled thru the suspension may be easily disposed of. A microscopic examination described below shows that the gelatinous precipitate is made up of thin plates which are greenest when they are thinnest.

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[1] Ann., 13, 155 (1835).

[2] Z. anorg. Chem., 73, 304 (1912).

[3] Gazz., 57, 232 (1927).

Hence anything which would break up the bluer aggregates of plates into thinner green plates should change the mass from blue to green. Two precipitates were made, both from oxygen-free solutions and both precipitated from 3 cc. of 1.55M KOH and 5 cc. of 0.83M $CoCl_2$, diluted to 20 cc. with oxygen-free water. Air was blown thru one and hydrogen thru the other. At the end of half an hour both were green, altho naturally the one thru which air had been blown was a little greener than the other. The precipitate was fine and homogeneous while that made from the same proportions of reactants but not stirred was heterogeneous and the coarser particles were blue laminae. Obviously the stirring hastens the change which would normally take place when the precipitate stands several days. Another explanation of this blue to green change is discussed on page 1265.

It is evident that oxidation does not always cause the blue to green change, altho it is easy to make the mistaken assumption that it does, since there is a change from blue to green when oxidation occurs.

Microscopic Study of the Green, Blue and Rose Precipitates

If a drop of cobaltous chloride solution is placed on a micro slide and a drop of the potassium hydroxide solution is added to the center of this drop, three different colored precipitates are produced—rose nearest the center in the presence of an excess of potassium hydroxide, green furthest from the center and between these a narrower ring of blue. All are laminar, gelatinous and amorphous. With × 210 magnification all three show irregular striations in the surface which in many cases appear like broken edges of unevenly piled laminae. There is also an apparent pitting over the surface of the yellow-red, the blue and the greenish-blue nearest the blue. This pitting is invisible with × 75 magnification but the striations remain very prominent. The green nearest the excess cobalt salt has a smooth glassy appearance, except for the striations, even with high magnification. When the cover glass is pressed down to disturb the precipitates, the yellow-red tends to break up into granular form; the blue breaks up into fine material which is then more yellow by transmitted light, or the large blue laminae may break into smaller laminar pieces which are still blue; the green tends to break into smaller laminae. This suggests that the pitting may actually be the first visible manifestation of crystal nuclei.

By changing the ratio of reactants very gradually an attempt was made to produce a homogeneous precipitate which would be entirely blue by transmitted light, since the above result indicates that there should be some intermediate concentration which produces the blue. A description of several typical precipitates follows:

1. 5.0 cc. of .83M $CoCl_2$ plus 4.8 cc. or less of 1.55M KOH, the precipitate shaken until homogeneous and a sample examined under the microscope at once. This gives a precipitate which is blue, with a slight greenish tinge, by reflected light. It consists of thin laminae ranging from grass green to bluish green by transitted light. The greater the excess of cobalt chloride, the more does the green predominate. The greener plates are thinnest as

evidenced by their greater translucence. Where two green plates overlap a bluer plate is apt to result. The same striations are evident, indicating that the laminae are piled. With × 210 magnification the same apparent pitting occurs in the bluer, heavier looking plates. With lower magnification the laminae present a glassy, smooth appearance. They are isotropic. Dichromatism may be partially responsible for the change in color with thickness from green to blue-green. This is a fairly common phenomenon described in detail by Wood,[1] wherein the transmitted color of a substance changes either with the thickness or with the intensity of the transmitted light. In this case, however, the laminae do not become bluer as the intensity of the illumination is decreased, as they should if the increasing blueness of the thicker plates were due to dichromatism.

2. 5.0 cc. of .83M $CoCl_2$ plus 5.0 to 5.3 cc. of 1.55M KOH, the precipitate mixed as before. (Molar ratio 1 : 1.87 to 1 : 1.99). The precipitate is a good blue, no greenish tinge, by reflected light. By transmitted light a few large irregular blue laminae are visible, occupying a maximum of five percent of the total area. The other ninety-five percent is fine, apparently laminar, green or bluish-green by transmitted light. Most of this blue, if not all, is due to reflection since if the precipitate is examined in a dark room with all light cut out except the directly transmitted beam, the fine material is green to yellow-green.

After thirty minutes the large laminae have changed from blue to green by transmitted light, while the fine material is yellow to greenish-yellow. The reflected color is still blue against a dark background.

3. 5.0 cc. of 83M $CoCl_2$ and 5.4 cc. of 1.55M KOH. This is slightly more than the potassium hydroxide equivalent to 5.0 cc. of cobalt salt, assuming that cobaltous hydroxide is formed. The entire area is blue by reflected light. A few large irregular laminae are blue by transmitted light, occupying a maximum of five percent of the total area. The rest is a fine, granular precipitate, essentially yellow by transmitted light.

After thirty minutes the large laminae are green and the fine granules are yellow to yellow-red. By reflected light the large laminae are still blue, while the fines are bluish-rose.

In the fresh precipitate, viewed between crossed Nicols, the large laminae are isotropic, showing as dark patches against a light gray background. This means that the fine granules are transmitting some light and must therefore be anisotropic. Since the magnification is not sufficient to distinguish the individual particles of the fine material, its behavior in this respect is rather deceiving. The whole field is a uniform gray and there is no variation in brightness as the stage is rotated, from which one would conclude that the granules are isotropic. With very minute crystals arranged in a haphazard manner, however, the brightness of the field would also remain constant during the rotation of an anisotropic substance, since the average number of crystals in the position of "extinction" would always be the same. The

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[1] Wood: "Physical Optics," 438 (1924).

fact which points to the anisotropy of the granules is that the whole field is a lighter shade than one composed of fine isotropic green particles under identical illumination and by direct comparison.

In all of the above descriptions the color by transmitted light is that shown when care is taken to eliminate all reflected light and all transmitted light incident at angles at or near the grazing angle. If light other than that transmitted at normal incidence is present, the color will be more blue due to the scattering of blue light, as discussed on page 1264.

Several important conclusions may be drawn from the data furnished by this microscopic examination.

1. The most significant is that a precipitate, only five percent or less of the area of which is blue by transmitted light, is a good blue by reflected light over the entire area. It is this reflected blue color, and not a blue transmitted color which, if it exists at all is only momentary, which must be accounted for to explain why freshly precipitated cobaltous hydroxide appears blue in bulk. This reflected blue is treated in detail on page 1260.

2. The precipitate which is blue by transmitted light for a short time is cobaltous hydroxide which has adsorbed some cobalt salt. If it were pure cobaltous hydroxide it would not turn green, since all the experiments indicate that some adsorbed salt is necessary to prevent the blue to rose change.

3. Freshly precipitated cobaltous hydroxide varies in color by transmitted light from green to yellow green, and these are the colors of thin, isotropic laminae.

4. The green color is not due to a basic salt, since it occurs when equivalent amounts of the reactants are used to precipitate cobaltous hydroxide.

5. The greater the proportion of potassium hydroxide, the more rapidly does the green precipitate age, changing in color first to yellow and then to rose, and from laminae to anisotropic granules. Therefore hydrous nickelous oxide and adsorbed cobalt salt may be assumed to inhibit crystal growth, or to stabilize the metastable laminar form. Again, since cobaltous chloride stabilizes the laminar form and since green plates are greener than piles of plates, a large excess of cobaltous chloride causes the plates to break up into thinner plates which exhibit an increasing tendency to appear green by reflected light as well as transmitted.

Recent work on beryllium hydroxide[1] offers an analogy to the behavior of cobaltous hydroxide. The former, freshly precipitated from dilute solution, is in thin hexagonal leaflets which later recrystallize in rhombic bipyramids. The change from laminae to granules is accomplished by heating or by allowing the precipitate to stand in contact with the mother liquor. It is apparently not uncommon for the precipitate of a hydroxide to be first laminar and change to a stable, granular form.

It remains to account for the precipitate which is blue by transmitted light. Its occurrence between the green and yellow-red precipitates when a

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[1] Fricke, Gottfried, Skaliks, Munchmeyer and Engelhardt: Z. anorg. Chem., **166**, 244 (1927).

drop of potassium hydroxide is added to a drop of cobaltous chloride suggests that the color depends on the relative amounts of reactants used. As subsequently shown, however, no precipitate entirely blue could be obtained by mixing gradually varying amounts of the reactants. The only part of such precipitates which was blue was a small percentage of the noticeably larger laminae which had not been mechanically broken during shaking. This suggests that the blue color is peculiar to the structure rather than being due to a difference in chemical constitution. Furthermore, if more dilute solutions are used so that the supersaturation of cobaltous hydroxide is not as great when the reactants are mixed, and therefore the laminae formed are not as thick, there are no large laminae present after shaking and none of the precipitate is blue by transmitted light. The structural explanation is, on the other hand, contradictory to the fact that after standing a short time these large blue laminae become green without any visible change in structure. Neither explanation harmonizes all the facts.

The behavior of solutions of cobaltous chloride suggests a more probable explanation. It has been pretty definitely shown[1] that when the cobalt atom is associated with six other groups the solution is red, while when associated with four other groups, it is blue. When the concentration of the cobalt ion in the blue solution is decreased, the solution becomes green. It is possible that when cobaltous chloride and potassium hydroxide are mixed without stirring, as in the drop experiment described, we are dealing with an intermediate stage between saturation and true precipitation, probably a very high degree of supersaturation involving the same interatomic or interionic relations as are manifest in the solution; and that the concentration of chloride ion controls the number of groups (ions, atoms or molecules) which will be associated with the cobalt atom, and thereby controls the color. The glassy appearance and lack of structural features in the isotropic precipitate formed under these conditions lend credence to this idea. Von Weimarn postulates several intermediate steps between supersaturation and the final orientation of the atoms in a precipitated crystal.[2] After agitating the precipitate, of course, these forces are broken down, resulting in the formation of the green, yellow or yellow-red precipitates, depending on the environment. If this be true, it is possible that the entire precipitate is momentarily blue by transmitted light when just the right proportions of reactants are used, but only the sturdier pieces survive in their original form. In a few moments even the larger pieces have turned green.

A comparison of the absorption spectra of the original green, blue and yellow-red precipitates with those of the corresponding colors of cobalt solutions would be helpful in deciding the validity of this analogy. Until that is done, no final explanation can be offered to account for the transmitted blue color.

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[1] See page 1247.

[2] Kolloid-Z., 44, 279 (1928).

X-Ray Diffraction Data for the Green, Blue and Rose Precipitates

X-ray diffraction patterns were obtained for the fresh blue[1] cobaltous hydroxide, the gelatinous green precipitate, rose cobaltous hydroxide and hydrous nickelous oxide. An account of the preparation of the samples and their description follows.

Blue Cobaltous Hydroxide.

This sample was prepared by adding 5.0 cc. of .83M $CoCl_2$ to 5.1 cc. of 1.55M KOH (molar ratio 1:1.91), mixing with hydrogen till homogeneous and washing on a filter paper with oxygen-free water in an atmosphere of hydrogen. Later it was found that it is not necessary to guard against oxidation, since it does not occur enough to alter the crystal lattice in any way. The washed precipitate was dried in vacuo over sulfuric acid to constant weight and analyzed for cobalt. It contained 60.3% Co, as compared with 63.4% cobalt calculated for pure $Co(OH)_2$. It should be emphasized that this "blue cobaltous hydroxide" when finally powdered for X-ray examination is neither blue, nor is it pure cobaltous hydroxide. It has been shown that adsorbed cobalt salt is necessary to stabilize the blue, and the analysis shows this to be present. In regard to color, the above preparation dries a good blue color, but turns gray when ground. If a greater excess of cobaltous chloride is used the tendency to turn green when ground increases. Nickelous hydroxide causes the same tendency. The gray powder obtained with the above mixture consists of a mixture of rose and green particles, giving an over-all color of yellow by transmitted light. Portions of the sample are anisotropic. The sample is designated "blue (gray)" in the discussion which follows.

Green, gelatinous precipitate.

5.0 cc. of 0.83M $CoCl_2$ were added to 2.0 cc. of 1.55M KOH (molar ratio 1:0.747) to which had been added 10cc. of oxygen free water. The precipitate was stirred with hydrogen until the green color developed and was then washed twice by centrifuging, removing the supernatant liquid, adding wash-water, stirring and centrifuging again. It was found that too thorough washing made the precipitate colloidal in every case. It was dried as was the blue and found to contain 53.0% cobalt. There was a considerable evolution of hydrogen chloride when it was dissolved in concentrated sulfuric acid.

This sample contains a large excess of cobaltous chloride which leads to the possibility of a basic salt being formed. On the other hand, we are interested in knowing the crystal structure with the impurity present, since the impurity controls the color. The powder is essentially an amorphous-looking mass, containing very few rose particles, and is more green and less yellow by transmitted light than was the blue described above. It is isotropic. It is designated as "green" in the following discussion.

A second green sample was prepared by adding 5.0 cc. of .83M $CoCl_2$ to 5.1 cc. of 1.55M KOH, thus eliminating the large excess of cobaltous chloride. It was found that, by washing this only once, it turned decidedly

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[1] For convenience, this fresh precipitate will still be referred to as "blue," its reflected color, whereas "green" will designate the precipitate which is green by reflected light.

bluish green after it was ground, being a good blue until then. The adsorbed potassium chloride probably has the same effect as the cobalt salt to a lesser extent. After drying in the usual way analysis showed 59.9% Co. This is designated "blue(green)" in the discussion.

Rose Cobaltous Hydroxide.

5.0cc. of .83M $CoCl_2$ were added to 7.0cc. of 1.55 M KOH (molar ratio 1:2.56) and the precipitate washed sufficiently to give 63.2% Cobalt and 19.4% H_2O, compared with 63.4% Cobalt and 19.2% H_2O calculated for pure cobaltous hydroxide. By transmitted light the powdered mass is more translucent than the blue or green and appears more crystalline. It is reddish-yellow by transmitted light and rose by reflected light, and is anisotropic.

Hydrous Nickelous Oxide.

A solution of nickelous nitrate was added to a moderate excess of potassium hydroxide and the precipitate washed as thoroughly as was the rose cobaltous hydroxide, and dried to constant weight for three days in vacuo over sulfuric acid. It was found to contain 59.6% nickel and 23.15% water.

The evidence regarding the composition of nickelous hydroxide is somewhat contradictory. Proust[1] and later L. Schaffner[2] determined it to be $4Ni(OH)_2.H_2O$. This is in agreement with the composition expressed by the analysis given above. On the other hand, Tower[3] shows definitely that $Ni(OH)_2$ may be prepared by drying a colloidal suspension of hydrous nickelous oxide for several weeks. It is probably merely a coincidence that the composition of the incompletely dried samples approximates a definite hydrate, and it is therefore more accurate to designate the sample prepared above as hydrous nickelous oxide. Whatever its formula it will have properties more like the freshly precipitated hydrous oxide than will one which has been dried for several weeks; and it will therefore be more significant in its causal relation to the stabilization of the laminar cobaltous hydroxide. The freshly precipitated hydrous nickelous oxide was laminar, and the dried powder isotropic.

The X-radiograms[4] were taken by the powder method of Davey.[5] An accurate determination of the structures was not attempted, merely a qualitative comparison of differences. A discussion of the patterns follows.

The crystal structure of rose cobaltous hydroxide has been determined as orthorhombic.[6] The blue (gray) sample was found to have the same lines in exactly corresponding positions, indicating that the arrangement of the

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[1] Neue allgem. J. Chem., (1805).

[2] Ann., 51, 168 (1844).

[3] J. Phys. Chem., 28, 176 (1924).

[4] The author is indebted to Miss M. K. Slattery, of the Dept. of Physics at Cornell University, who obtained the X-radiograms for all the samples; and to Dr. Marie Farnsworth, of New York University, who proffered the X-ray equipment of that laboratory for further investigation of the problem.

[5] Gen. Elec. Review., Sept. (1922).

[6] Natta and Reina: Atti. Accad. Lincei, (6) 4, 48 (1926).

atoms and the size of the unit cell are the same in both. Incidentally, it also shows that the adsorbed cobalt salt does not go into the crystal lattice, since it would be expected to cause a shift in the lines. The intensity of the lines from the gray powder is less than that of those from the rose, indicating that the concentration of the crystals giving these lines is less. If it is recalled that the gray powder consisted of a mixture of green and rose particles, the comparative intensities of the lines implies that the pattern obtained is simply that of the rose particles present in large amount in the gray, and that the green particles are amorphous. Since only the rose pattern is present on the gray film, the green particles, if crystalline, must be identical with the rose and their pattern superimposed on the rose pattern. But in this event the two intensities would not vary.

In order to try to eliminate this rose pattern and get the true structure of the blue, if there be one, the blue(green) preparation was examined. Since that one turned green when powdered whereas the blue(gray) turned gray, it must contain much less of the rose. The result of this comparison is brought out in Table III.

TABLE III

Rose $Co(OH)_2$		Blue(green)		KCl[1]	
Ångströms	Intensity	Ångströms	Intensity	Ångströms	Intensity
4.65	4	4.80	4		
		3.17	4	3.12	15
2.76	3	2.78	3		
2.37	4	2.40	4		
		2.24	2	2.21	10
		1.82	1	1.81	3
1.778	3	1.79	2		
1.590	3	1.595	2	1.57	1
1.505	2	1.510	2		
1.423	2	1.416	1	1.403	2
1.375	1	1.380	1		

The intensities were estimated by inspection and assigned to one of four different values, number four being most intense and number one all but invisible. The numbers bear no relation to those listed for KCl. The table shows that the blue(green) pattern contains all the lines of the rose pattern and some extra ones. These extra ones are the strongest lines of potassium chloride, which was not thoroughly washed from the precipitate. The lines do not match exactly and is was suspected that perhaps some potassium chloride was actually adsorbed and altered the cobaltous hydroxide lattice somewhat. To check this, another picture was taken of the rose and blue (green) side by side on the same film. The lines were exactly the same spacing as indicated by their continuity.

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[1] Davey: Phys. Rev., (2) **21**, 152.

It must be remembered that both the blue(gray) and blue(green) are samples which have been dried and powdered. Neither throws any light on the condition of the fresh gelatinous precipitate. Since cobaltous chloride in greater excess stabilizes the laminar structure, the green powder containing a greater amount of cobaltous salt should more nearly represent the condition of the fresh precipitate. The position of the lines are given in Table IV.

TABLE IV

Ångströms	Intensity	Ångströms	Intensity	
2.78	1/2	1.60	1/2	blurred band
2.39	1	1.51	1/2	
1.79	1/2			

There are only three definite lines present, two of which are all but invisible. It is significant that these lines correspond to the strongest on the rose pattern as recorded above; but they are very indistinct even tho the sample was exposed to the X-rays much longer than was the rose. Evidently crystallization has just started, and it is safe to conclude that the fresh green precipitate is truly amorphous, and that in the fresh blue precipitate crystallization is not as far along as it is when the pattern for the blue is obtained. Clark states[1] that this method is the most sensitive for detecting the beginning of crystallization as a gel ages.

There are only two very faint and blurred lines on the diffraction pattern for hydrous nickelous oxide, located at 2.72 Å and 1.56 Å., the latter being very much weaker than the former. If these mean that crystallization is just beginning it is interesting to note that hydrous nickelous oxide remains amorphous for some time without the stabilizing influence of any added salt. Tower[2] found that nickelous hydroxide was isomorphous with cobaltous hydroxide; but he was dealing with a sample which had been subjected to more drastic treatment, as explained above. There are other possible interpretations of this pattern. Wyckoff[3] says that so-called semi-liquid crystals, in which atoms are oriented in only two directions, do not give a definite diffraction pattern but show one line and sometimes a repetition of this line in a higher order. Atoms oriented in two directions suggest thin plates. It has since been shown[4] that such a pattern does not necessarily indicate a semi-crystalline substance, but does mean that the substance is laminar. Also, Clark says:[5] "The mesomorphic phases represent the primary orientation of the molecules—this results in swarms of minute colloidal crystallites which combine with a growing nucleus to give the completed crystal." Thus, regardless of which interpretation is the correct one, the hydrous

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[1] "Applied X-rays," 179 (1927).

[2] J. Phys. Chem., 28, 176 (1924).

[3] "The Structure of Crystals," 379 (1924).

[4] Wyckoff, Hunt and Merwin: Science, 61, 613 (1925).

[5] "Applied X-rays," 176 (1927).

nickelous oxide is laminar and is either amorphous, or is just beginning to crystallize; which means that it is amorphous when freshly precipitated.

The X-ray diffraction data, therefore, bring out the following facts to corroborate and supplement the information obtained with the microscope. Freshly-precipitated, green or blue, cobaltous hydroxide is amorphous. Rose cobaltous hydroxide is crystalline. In that sense the two differ in crystal structure. They do not follow the analogy of red and blue cobalt solutions, however, nor should they be expected to, since the true colors in this case are rose and green, the blue being only a reflected color.

There is no intermediate crystal form of cobaltous hydroxide to account for a color change; only the final rose pattern exists. Hydrous nickelous oxide, when freshly precipitated, is laminar and amorphous and therefore stabilizes the laminar form of cobaltous hydroxide and inhibits crystal growth, retarding the blue to rose change.

Just why cobaltous hydroxide in laminar form should be green and in crystalline granular form rose, is not known. It may at least be pointed out that there are numerous familiar examples of the manner in which the size and shape of masses affect their hues by transmitted light. Hedvall[1] investigated a number of metallic oxides which existed in two different colors under different conditions and found that the crystal structures of the two colors were in most cases identical. A closer scrutiny showed that the change in color in several cases was accompanied by a change from a laminar to a granular structure. In the present case, however, it is possible that the difference in color is affected to a greater extent by the fact that one is amorphous and the other crystalline. The difference in orientation of the atoms or ions under these conditions would give rise to differences in interatomic or interionic forces which would doubtless affect the color absorbed, if that color is an electronic effect.

The Reflected Blue of Cobaltous Hydroxide

This blue is the reflected color of a precipitate which is essentially green to yellow by transmitted light. It has been shown that the contribution to this color of the small amount of precipitate which is blue by transmitted light is almost negligible. Apparently the study of Optics offers only two possible explanations to account for the true reflected color. It may be the surface color of a substance showing selective reflection, or it may be one of several types of structural blue.

Selective reflection, or surface color, is discussed in detail by Wood[2] and more briefly by Bancroft.[3] When some or all of the light which is most strongly absorbed by a substance is reflected strongly from a polished surface of the substance, the phenomenon is known as selective reflection. The result will be a body, or transmitted color, approximately comple-

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[1] Z. anorg. Chem., **120**, 338 (1922).

[2] "Physical Optics," 409 (1924).

[3] "Applied Colloid Chemistry," 252 (1926).

mentary to the surface, or reflected color. Thus, magenta is red by transmitted light and green by reflected light. Many other cases are known. Michelson[1] has listed the chief characteristics by which selective reflection may be recognized:

"1. The brightness of the reflected light is always a large fraction of the incident light, varying from 50% to nearly 100%.

"2. The absorptionis so intense that metal films are quite opaque even when their thickness is less than a thousandth of a millimeter.

"3. If the absorption varies with color, that color which is most copiously transmitted will be part of the incident white light which is least reflected—so that the transmitted light is complementary to the reflected."

The precipitate of cobaltous hydroxide does not satisfy any one of the three points. The reflected blue is not as bright as the first statement would indicate. The green laminae are far from opaque, being very translucent and almost colorless under more intense illumination. Green and blue are not complementary, altho the disagreement on this point is not serious because the transmitted color is usually yellow-green or yellow. On the first two points, however, it is evident that the blue is not a surface color.

There are several kinds of structural blue; grating blue, thin-film blue, the blue of colloidal particles and Tyndall blue.

The blue is not a grating color. The striations on a diffraction grating must be in a regular arrangement, while in the present instance both the striations and the laminae are entirely irregular, both in direction and spacing. Also, the hue does not change as the angle of incident light changes.

The blue is not a thin-film color. The laminae are not thin enough to cause interference colors and the blue does not exhibit the optical properties of thin-film colors: notably, it does not change hue as the angle of incident light changes.

The blue is not due to finely divided particles of cobaltous hydroxide for several reasons, which follow:

1. There is no gradual change in color, as there should be if the particles changed in size from small blue to large rose. The blue to rose change, thru violet, seems to satisfy this but the violet precipitate is found to consist of a mixture of green laminae and rose granules and no violet as such. Furthermore, when a deep blue ages to a light blue there is certainly an increase in particle size, but there is no change in color.

2. If the blue were the color of finely divided particles they should be blue by transmitted light as well as by reflected light. There are some cases where metal sols are one color by reflected light and another by transmitted light, but these are special cases of selective reflection involving resonance,[2] and are therefore eliminated for the same reasons that selective reflection has

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[1] Phil. Mag., (6) **21**, 564 (1911).

[2] Wood: Phil. Mag., (6), **38**, 98 (1919; Kossonogoff: Physik. Z., **4**, 208, 258 (1903).

been eliminated. Recently, Bancroft has suggested that the blue reflected color of a gold sol, in which the particles themselves are yellow or brown, is a Tyndall blue.[1]

3. The following experiment is significant. A fresh blue precipitate prepared by adding a slight excess of cobaltous chloride to potassium hydroxide was centrifuged. the mother liquor poured off, distilled water added, the precipitate stirred and centrifuged again. After the second repetition the sediment consisted of two layers, a rose one on top and a blue layer beneath it. Of course the rose layer is composed of the smaller particles. Since crystallization is inhibited by cobaltous salt, the smaller aggregates which can be most quickly washed free of cobaltous chloride will crystallize in the rose form sooner; while the larger aggregates will remain blue and go to the bottom. If this precipitate be washed several times more in a similar manner it will not settle out, nor can it be centrifuged out, but will remain in suspension several weeks, a fair indication that the particles are pretty small. These suspended particles are rose, not blue, but they are small enough to give a weak Tyndall effect and scatter blue light.

By a process of elimination, then, we come to a consideration of the blue as a Tyndall blue; which is a blue scattered by small particles, the size of which is of the order of the wave-length of blue light.

Mason[2] has listed six properties of a Tyndall blue and of the medium which may scatter it. Some of these properties have actually been observed in the blue precipitate; most of the others may be indirectly deduced. They are considered below.

1. "Particles, or other optical inhomogeneities, of a refractive index different from that of the medium which surrounds them. No color if refractive indices are not different."

It has been shown that the fresh green gelatinous precipitate is amorphous and the final rose precipitate is crystalline. The blue is an intermediate color. There must also be an intermediate stage from the structural standpoint when crystallization is just starting and the crystal nuclei would be of the proper size to scatter blue light. It is very unlikely that the refractive indices of the amorphous and crystalline forms would be the same. A clear picture of what is happening during crystallization is important in following the discussion. It is logical to assume that the crystal nuclei form within the amorphous green laminae and grow while embedded therein until they become of sufficient size to break apart from this matrix and appear as rose granules. The crystals are probably rose by transmitted light throughout their growth. The process is analogous to the devitrification of a combustion tubing when crystal nuclei of glass form within the glass itself,[3] and such a tubing is known to scatter a Tyndall blue.

2. "Dimensions of these particles of the order of the wave length of blue light (something less than 0.6μ)."

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[1] Private communication.

[2] J. Phys. Chem., 27, 224 (1923).

[3] J. Phys. Chem., 27, 222 (1923).

As suggested above, at some stage in their growth the nuclei must be the right size to scatter blue. It might be argued that the X-ray diffraction pattern of the blue should indicate this by a broadening of the lines on the pattern, since it is known that such broadening does occur as particle size decreases. It has been shown,[1] however, that sharp lines are obtained from particles larger than 10^{-6} cm. or .01μ., so that particles of the order of .6μ would give a sharp pattern.

3. "Depth or shade of blue dependent on size of particles. Large particles give whitish blue or white."

As has already been noted, with the proper proportions of reactants the deep blue, gelatinous precipitate ages and becomes gradually more white—a lighter blue. This fading parallels exactly the color change in the sample of Tyndall blue prepared by heating the Jena combustion tubing. The heating causes the partial devitrification of the glass, the crystals being largest in the portion which was hottest. The reflected color is nearly white at this point, while the blue becomes more intense toward the portion which was cooler; that is, the tube is bluer where the particles causing the scattering are smaller. Of course this analogy does not prove the presence of a Tyndall blue, but it is certainly significant, for if the precipitate is amorphous when first formed and crystalline when the diffraction pattern is obtained, a gradual growth of crystals must occur. The same fading of the blue color occurs in the blue to rose change, but the appearance of the rose color, which is naturally lighter, masks it.

4. "Scattered light blue, transmitted light reddish. Blue seen only when transmitted light is cut off."

When a very thin layer of the blue precipitate is examined on a micro slide, there is no evidence of any transmitted reddish beam. When the freshly precipitated suspension is placed in a glass cell 5 mm. thick and a strong beam of light passed thru it, the transmitted color is decidedly reddish. Of course any fine suspension will show the Tyndall effect, but it must be remembered that in this case the suspension is of gelatinous laminae, large enough to settle out rapidly. These would not, in themselves, give the effect and the scattering must therefore be due to some structure, such as crystal nuclei, within the laminae themselves. The following series of precipitates were formed by adding the indicated amounts of 1.55M KOH to 5.0 cc. of .83M $CoCl_2$, shaking until homogeneous. A little was then examined in the absorption cell:

		Color	
cc. KOH	Reflected	Transmitted (diffuse)	Transmitted (direct)
4.7	greenish-blue	green	green
4.8	blue	greenish-blue some red	green and red
4.9	blue	greenish-blue more red	green and red
5.0	blue	distinct reddish-blue	green and red

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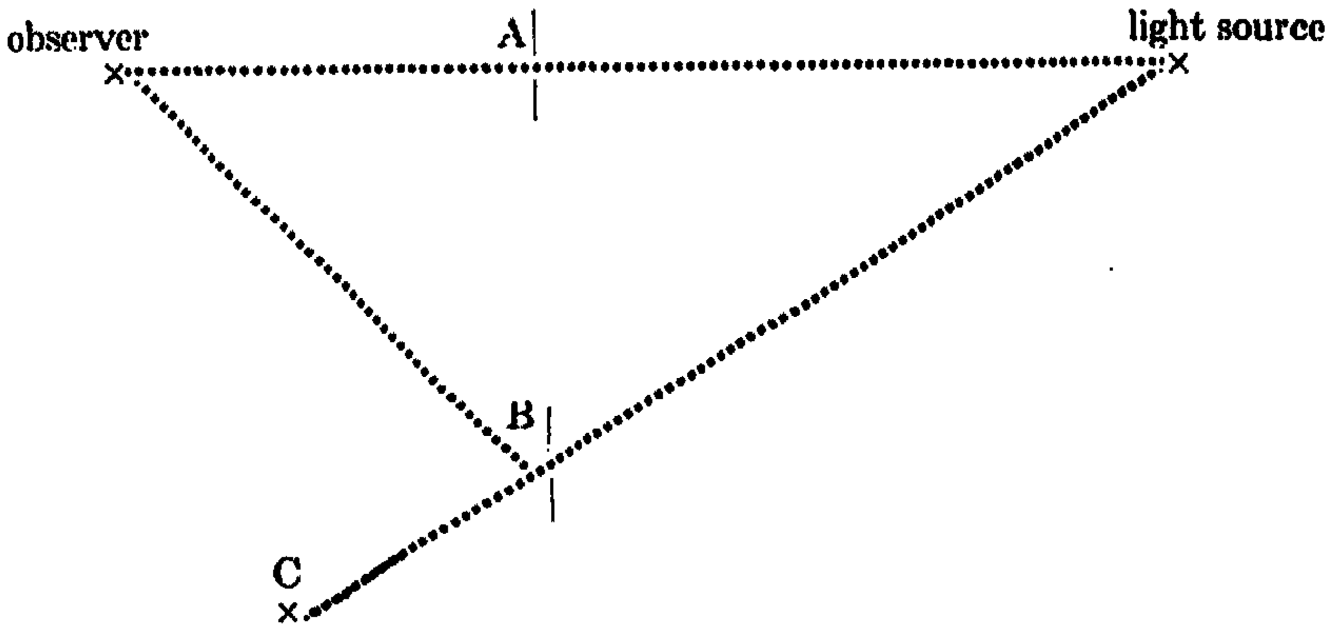
[1] Clark: "Applied X-rays," 181 (1927).

It is significant that as the ratio of reactants is changed the first suggestion of a reddish tinge in the transmitted light corresponds exactly with the first appearance of a lasting blue by reflected light.

If the cell is simply held between the eye and a fairly large source of light, the transmitted colors in the third column are observed; and the more concentrated the solution, the more blue is the precipitate. There is not a great difference between the hues by transmitted and reflected light. If the beam of light is sharply defined, however, by wrapping the cell in black paper and allowing the light to be transmitted thru a small window (1 cm. square), thence thru the solution and out a similar window opposite the first, the transmitted light is a mixture of red and green as noted in column four of the table. The results in column three are obtained when the incident light is diffuse, so that much of it passes thru the precipitate at such an angle that the observer sees the scattered blue light rather than the transmitted beam. As the cell is moved nearer the source, the amount of diffuse light decreases and the blue color gives way to the red and green. The intensity of the transmitted light also increases, which might suggest dichromatism as the cause of the change in color. But if the sharply defined beam is used, there is no change in the hue as the intensity of the transmitted light is varied, which of course rules out dichromatism.

The following experiment shows definitely that the apparent transmitted blue when a diffuse light source is used is merely blue scattered from light which is incident at angles varying widely from the normal. The precipitate, blue by diffuse light, is placed in the cell and the transmitted light defined by the windows described. When the opening thru the cell is in position A in the following diagram, the transmitted light is red and green. As the cell is moved to position B, the light coming thru grows more blue, until at B it is a good blue, as pure a blue as is obtained in the fresh blue precipitate by reflected light. The experiment should be done in a dark room.



In the ordinary sense the light is transmitted, since it is shining thru the hole in the dark screen. Actually the observer sees the scattered light at or near right angles to the transmitted beam. If the observer move to position C, the color transmitted is again red and green. It is actually possible to distinguish red and green with the naked eye: but the absorption spectrum also bears out this observation, showing an absorption band including all the yellow and part of the red and another band including all of the blue. The spectrum also indicates that the red transmitted increases as the proportion of potassium hydroxide increases. With more dilute solutions or thinner cells, the proportion of red decreases and the green body color predominates. When laminae are examined under the microscope the layer is so thin that there are not enough particles in the path of the normal beam to scatter the light and so the green body color of the amorphous cobaltous hydroxide is manifest, rather than the reddish Tyndall beam.

5. "Scattered light polarized, vibrations in plane normal to the direction of the incident beam. Completeness of polarization dependent on size of particles."

The blue light scattered from the precipitate has been found to be polarized in the proper direction. The completeness of polarization with size of particles was not tested.

6. "Intensity of scattered light inversely proportional to fourth power of wave length." This point was not investigated.

Another criterion for a structural Tyndall blue which is noticeably satisfied by the blue cobaltous hydroxide is that it is most intense against a dark background.[1]

If the blue of freshly precipitated cobaltous hydroxide is a Tyndall blue it naturally follows that the light blue, aged, granular precipitate is also a Tyndall blue. A thin layer of this is slightly reddish-yellow by transmitted light. The reflected blue is plane polarized. The existence of optically unhomogeneous particles has been postulated. The blue is more intense against a dark background.[1] It has also been stated that this aged blue may turn green when dried; or if blue when dried, it may turn green instantaneously when ground. The resulting grayish-green powder is found to consist of green and rose particles. Bancroft[2] has attributed the blue color of some slags, which turn a dirty green when ground, to their structure.

If the blue color is scattered by crystal nuclei, it is necessary to account for the change to green of the deep blue precipitate which is first formed in the presence of an excess of cobaltous chloride. As previously stated, this deep blue actually has a greenish tinge and a detailed inspection shows that there are large blue laminae distributed thru a finer green precipitate giving the blue color overall. A few of these blue laminae persist after prolonged stirring. Some of them may be blue by transmitted light and these have been discussed elsewhere. The rest are laminae formed under conditions which would permit the formation of crystal nuclei. During the actual mixing of the reactants there would be spots where the excess of cobaltous

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[1] Mason: J. Phys. Chem., 27, 223 (1923).

[2] J. Phys. Chem., 28, 12 (1924).

chloride was not sufficient to prevent this, since the reactants are not homogeneous at the instant they are mixed. Subsequent stirring breaks down these laminae, liberates the nuclei, and much of their light scattering effect is lost due to their greater distribution and dilution, altho since the change, amorphous green to crystalline rose is irreversible, the nuclei must still be present.

The structural properties of the precipitate, to which the Tyndall blue may be definitely attributed, have not been directly detected. Apparent "pitting" of the laminae has been observed in all but the green precipitate; that is, in precipitates which are blue or which have been blue. It is very likely that crystal nuclei cause this pitted appearance, altho when observed they have already grown too large to scatter blue light. Their presence in the amorphous matrix lends further support to the idea that a large number of smaller nuclei, similarly distributed, are present along with them and also at an earlier stage. The irregular striations might also be expected to scatter some blue light, but in the crystal nuclei lies the most probable cause of the Tyndall blue.

Since the particles of the order of .6μ have not actually been observed, one is perhaps justified in questioning the conclusion drawn; but because the optical requirements for a Tyndall blue are satisfied almost completely, and particularly because the optical properties of the blue cobaltous hydroxide are in decided disagreement with those of other forms of structural blue, it may be stated fairly definitely that the blue color of the fresh precipitate is a Tyndall blue.

Attributing the blue color to the scattering effect of crystal nuclei sounds very much like a confirmation of the suggestion that the difference in color of the blue and rose is due to a difference in the size of the particles, the blue being the smaller. Postulating fine particles which scatter a Tyndall blue, however, is quite different from assuming the blue color to be due to finely divided cobaltous hydroxide which is itself blue.

Section II. The Aged Precipitates, Green, Blue and Rose

When 4.0cc. or less of 1.55M KOH are added to 5.0 cc. of .83M $CoCl_2$ (molar ratio 1.49:1), the blue gelatinous precipitate changes to a green gelatinous precipitate as usual, and the latter ages gradually. It settles, assumes a granular appearance and changes to a light green, then to blue and finally to rose. The progress of this change and the conditions controlling it are illustrated in the following table.

Varying amounts of 1.55M KOH were added to 10.0cc. of .83M $CoCl_2$, and the mixture stirred by bubbling hydrogen thru it for ten minutes. It was found that subsequent aging was more rapid when the time of stirring was increased and also when the temperature was increased.

The volumes are roughly estimated by comparing with the one of greatest volume taken as unity. The table brings out several points:

1. The aging is accompanied by a change of color from green to blue to rose and by a mechanical breaking down of the gelatinous precipitate to form a

granular one, as shown by the decrease in volume. It would be expected, therefore, that long mechanical stirring would hasten the aging, and it does.

2. The rate of aging increases as the ratio $CoCl_2$:KOH increases. This is evident throughout, but is emphasized particularly by the appearance of the rose in No. 1 after six days, while it did not appear in No. 4 for fifty days.

3. No appreciable aging, as evidenced by color change and settling takes place with excess cobalt salt present in amounts less than 1 mol $CoCl_2$:1.5 moles KOH. (the concentration of No. 4)

TABLE V

No.	cc. KOH	Description after 3 days		6 days		50 days	
		Vol.	Color	Vol.	Color	Vol.	Color
1	5.0	1/3	blue, no green on top	1/4	rose layer top, blue at bottom	1/8	all rose
2	6.0	3/4	light green	1/3	blue-green on top	1/4	rose, green on top
3	7.0	7/8	green as above	2/3	blue, green on top	3/8	rose, green on top
4	8.0	1	green, looks fresh gelat.	1	green, looks fresh	7/8	slightly blue green at bottom, middle layer rose, green top
5	9.0	1	green, looks fresh	1	green, looks fresh	1	green, looks fresh
6	9.6	7/8	bluish at bottom, top green	7/8	bluish at bottom, top green	2/3	yellow-green
7	10.0	1/2	blue	1/2	gray-green	1/2	brown-green

4. The aging results not only because a greater amount of cobaltous chloride is originally adsorbed, but it also results from the precipitate standing in contact with cobaltous chloride solution. This is clearly shown in No. 1. after six days there was a rose layer nearest to the solution, which is further advanced than the blue at the bottom. This rose subsequently worked down. In a separate experiment, the precipitate was formed in the same proportions, but the excess cobalt salt was immediately washed out with potassium chloride. This precipitate, left standing for two months, did not change from the original green color (except for a brownish tinge due to oxidation), and did not become granular; that is, no aging occurred.

5. The tendency to turn brown or yellow in Nos. 6 and 1 is due to partial oxidation. In Nos. 2 and 3 some oxidation of the surface layer took place before the aging started, producing a green layer which did not age later.

The three stages of the aging precipitate—green, blue and rose—were examined with a microscope. They are all made up of fine particles with only an occasional plate of any size. The frequency of occurrence of larger plates depends on the length of time the precipitate was stirred. The stirring helps break the plates, altho they tend to break eventually anyway. The few plates left are portions which have not undergone any aging. They are isotropic. The small particles of these aged precipitates are very different in appearance from those in the fresh precipitates. The latter were comparatively transparent, while the former are quite opaque, fleecy masses made up of agglomerates of very fine particles. This is true of Nos. 1 thru 4 in table, examined after fifty days. No. 5 appears exactly like a freshly prepared precipitate, consisting of transparent, green laminae which are isotropic. No. 4, which has settled some, is fleecy looking and transmits some light between crossed Nicols, altho not as much as the rose of No. 3, which is definitely anisotropic. The transmitted and reflected colors of the precipitates as they age are listed in Table VI.

TABLE VI

Color in bulk	By transmitted light	By reflected light
green	yellow-green (a few red spots)	slightly bluish-green
blue	yellow (red and green mixed)	clear powder blue
rose	yellow-red (some green patches)	slightly bluish-red to red

Of course the proper mixture of red and green will transmit yellow and the blue is made up of such a mixture. The blue, then, is an intermediate stage in the change from green to rose. This merely recalls the actual change of color observed during aging, but it also indicates that the blue is not inherently different in itself, merely a mixture of the green and rose. The green is a true absorption color, transmitting and reflecting the same color. The rose is likewise an absorption color. It is also evident that the green is amorphous and the rose crystalline, while the blue is again a Tyndall blue made up of a mixture of the two. The same number of criteria of a Tyndall blue were not applied here as were with the fresh blue precipitate, but this aged blue does always turn green or gray when its structure is disturbed by drying or powdering. It is quite possible that small crystal nuclei are responsible for the blue color. The precipitates begin to show a bluish tinge by reflected light (as can be seen from the above table) as soon as they begin to settle out and crystallize.

X-ray diffraction patterns were obtained for the green, blue and rose. The samples were all prepared by adding 7.0 cc. of 1.55M KOH to 10.0 cc. of .83M $CoCl_2$ plus 10.0 cc. of water and stirring ten minutes with hydrogen. Only the time of aging was varied to obtain the different colors. These precipitates all contain more adsorbed cobalt salt than do the fresh ones, and analysis indicates between 54 and 55% cobalt in each. The patterns obtained are given below. Since the analysis indicates we are not dealing with pure $Co(OH)_2$, the possible impurities are listed in Table VII for comparison.

TABLE VII

Green		Blue		Rose		$CoCl_2$ anhyd.		$CoCl_2$ $6H_2O$		$Co(OH)_2$		KCl	
Å	Int.	Å	Int.	Å	Int.	Å	Int.	Å	Int.	Å	Int.	Å	Int.
								4.39	5				
3.8	blur					3.8	blur	3.62	1b				
3.2	2	3.18	2b			3.05	3	3.16	1b			3.12	15
		2.88	3b	2.89	2			2.89	4				
2.82	2b	2.79	5	2.80	4			2.75	5	2.76	3		
2.72	1b							2.68	1				
2.39	2							2.40	4	2.37	5		
2.31	3	2.28	5	2.29	5			2.32	3				
2.24	1	2.22	1	2.22	1			2.16	3			2.21	10
		2.14	1	2.15	1			2.08	5				
		1.963	2	1.965	1								
1.84	1	1.826	3	1.825	3			1.85	1				
1.79	1	1.767	2	1.765	1	1.79	5	1.815	2			1.81	3
1.72	1	1.712	4	1.713	4	1.708	3	1.778	2	1.778	3		
		1.625	2b	1.626	2b			1.744	2				
1.59		1.550	3b	1.550	2			1.718	1	1.590	3	1.56	1
1.51	blur	1.522	3b	1.520	2			1.685	3	1.505	2	1	

All these patterns listed except the green contain more lines corresponding to less than 1.5Å but they are faint and of no significance in the present discussion. A letter "b" after the intensity number signifies that the line was blurred, making the reading inaccurate. The estimated intensities are from five to one, five being the strongest.

Certain definite conclusions may be drawn from the above comparison. First, the structure of the rose corresponds to that of the blue as would be expected, since the blue was found to be a mixture of rose and the amorphous green. Secondly, this rose pattern is different from the pattern of pure cobaltous hydroxide, altho the blue and rose colors match perfectly in appearance. It is well known that when two or more substances are mixed, each substance in the mixture will produce its own crystal diffraction pattern, independently of the others, provided that it is present in sufficient concentration, say 5 to 10%. Therefore if the rose pattern contains lines which cannot be found in the pattern of cobaltous hydroxide or those of any of the impurities which might be present (namely $CoCl_2.6H_2O$, $CoCl_2$, or KCl), it is definite evidence that a different compound is present. A detailed comparison of the pattern for the rose aged precipitate with the others recorded shows that to be the case. In making such a comparison the relative intensities of the lines must be kept in mind. Thus, we find a line at 2.89Å on the hydrate pattern which corresponds with a line (2.89Å) on the rose pattern. But if this line of the hydrate with an intensity of 4 is present on the rose pattern, then lines 2.08 and 1.79 with intensities of 5 should be still more evident on the rose pattern. Since neither of these lines do occur on the rose, it means that line 2.89Å on the rose is not due to adsorbed hydrate, but is a line of the rose compound which merely happens to coincide with the hydrate line. Following this reasoning with all the most prominent lines on the rose pattern, we find them to be unique, indicating the presence of a different compound. This is doubtless a basic salt of cobalt chloride. Apparently the only basic salt recorded in the literature is one corresponding to the formula $CoCl_2.3\ CoO.3\ 1/2\ H_2O$, precipitated from hot ammonia added to boiling cobaltous chloride and of peach-blossom color.[1] The rose precipitate may be a different one and is being more carefully investigated at the present time.

The pattern for the light green granular precipitate taken before aging had progressed very far is interesting. The lines are few and none too definite even tho the sample was given a longer exposure than the others. That in itself indicates that crystallization is just starting. Considering the lines in detail: the blur at 3.8 Å corresponds to the strongest line (also indistinct) of the anhydrous cobalt chloride pattern. The weak line at 3.2 corresponds roughly to the strongest line for potassium chloride. The remaining lines of the light green pattern are tabulated against the most prominent lines of the rose basic salt and pure cobaltous hydroxide in Table VIII.

TABLE VIII

Light green		Rose basic salt			$Co(OH)_2$	
Å.	Int.	Å.	Int.		Å.	Int.
2.82	2 (blur)	2.79	5			
2.72	2 (blur)				2.76	3
2.39	2				2.37	5
2.31	3	2.29	5			
2.24	1	(2.22	1)	(2.21 strong on KCl)		
1.84	1	1.826	3			
1.79	1	(1.765	1)		1.778	3
1.72	1	1.713	4			
1.59	blurred band				1.590	3
1.51					1.505	2

Of course, the lines do not correspond exactly, but considering the indistinctness of the light green pattern, the correspondence is more than a coincidence. The relations of the intensities of the lines is most conclusive, however. The two most distinct lines on the green pattern, those at 2.39Å and 2.31 Å, are taken care of by the strongest line on the cobaltous hydroxide and the rose basic salt respectively; and *all* the lines of both the basic salt

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[1] Habermann: Monatshefte, 5, 432.

and the hydroxide with intensities of three or greater occur on the green pattern. It is quite evident that the green itself is amorphous but contains small amounts of the crystalline basic salt and crystalline cobaltous hydroxide, and perhaps some potassium chloride. Certainly the rose basic salt is the only crystalline compound formed during aging. It is easy to account for the presence of these two crystalline substances in the green. The rose basic salt, as suggested by the microscopic examination, has already begun to form. Cobaltous chloride inhibits the formation of crystalline, rose cobaltous hydroxide, but the action is irreversible. So the small amount of crystalline cobaltous hydroxide present in a fresh green precipitate, as shown by its diffraction pattern in Table IV, will naturally remain as such in the aged precipitate.

The significant thing shown by the X-ray data is that the crystalline basic salt is formed only after the precipitate has stood some time in contact with cobaltous chloride solution. At first the basic salt, if formed at all, is amorphous. It is more likely that cobaltous chloride is first adsorbed by the green, amorphous cobaltous hydroxide and then slowly combines with it on standing. It has recently been noted by Neville[1] that during the hardening of plaster of Paris the water is first adsorbed and later combines to form the hydrate, so similar action between cobaltous chloride and cobaltous hydroxide would not be unique.

Summary

All the colors resulting from the interaction of a cobaltous salt with potassium hydroxide have been shown diagrammatically on page 1248. The conditions controlling each of the changes indicated there have been defined. These conditions, together with a microscopic study of the changes and of the several products, and a study of the products by means of X-ray diffraction patterns lead to the following results.

1. Freshly precipitated cobaltous hydroxide is green to yellow-green by transmitted light. It is gelatinous, laminar in appearance and amorphous. In this form it is metastable.

2. The blue of freshly precipitated cobaltous hydroxide is essentially a reflected color. By a process of elimination it has been shown that it is probably a Tyndall blue scattered by small crystal nuclei which form within the amorphous matrix as the gelatinous precipitate ages to the crystalline form. Its optical properties have been compared in detail with those of a typical Tyndall blue.

3. The freshly precipitated cobaltous hydroxide tends to change to the familiar rose cobaltous hydroxide which is granular in appearance and crystalline. It is the stable form.

4. There is no other crystalline form of cobaltous hydroxide produced under the conditions of the experiment. The aged, light blue precipitate is crystalline but its structure is exactly the same as that of the rose. The blue of the aged precipitate is also a structural color.

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[1] J. Phys. Chem., 30, 1037 (1926).

5. Adsorbed cobaltous chloride inhibits crystal growth and therefore favors the formation of the green precipitate and hinders the formation of the rose. It does not combine chemically with the cobaltous hydroxide.

6. Freshly precipitated hydrous nickelous oxide is laminar and amorphous and therefore tends to stabilize the laminar, amorphous cobaltous hydroxide.

7. It is not true that the blue to green change of freshly precipitated cobaltous hydroxide is due to oxidation.

8. A very small proportion of a fresh cobaltous hydroxide precipitate is blue by transmitted light. This cannot be accounted for, altho a tentative explanation is offered.

9. When cobaltous hydroxide is added to potassium hydroxide in amounts greater than 1 mol $CoCl_2$: 1.5 mol KOH and the precipitate stands in the mother liquor, aging occurs and the color of the precipitate changes from green to blue to rose.

a. The final rose precipitate is not cobaltous hydroxide or a mixture of cobaltous hydroxide with cobaltous chloride, but is a basic salt of cobalt.

b. The blue precipitate is a mixture of the rose and the green and the color is structural blue.

c. The first green precipitate is essentially amorphous, containing small amounts of crystalline cobaltous hydroxide and of the crystalline basic salt. It is not a second crystalline form.

d. The final rose basic salt is the only crystalline product formed under the conditions of the experiment.

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NEW BOOKS

Colloid Chemistry. *Edited by Jerome Alexander. Vol. II. 23 × 16 cm; pp. 1029. New York: Chemical Catalog Company, 1928. Price: $15.50.* This book contains articles dealing with biology and medicine. The authors and subjects are: Jerome Alexander and C. B. Bridges, Some Physico-Chemical Aspects of Life, Mutation, and Evolution; Stéphane Leduc, Solutions and Life; A. L. Herrera, Plasmogeny; Sir William Bragg, Colloids and X-Rays; A. deG Rocosolano, The Ageing of Colloids; N. R. Dhar and D. N. Chakravarti, Hydration and Viscosity of Sols in the Presence of Electrolytes; Fil. Bottazzi, The Surface Tension of Colloids with Special Reference to Protein Colloids; J. H. Yoe, Nephelometry; J. H. Yoe, Colorimetry; E. T. Wherry, The Desirability of sometimes stating Reactions in Terms of Concentrations rather than pH; Fil. Bottazzi, The Colloidal Systems of the Living Organisms; Wolfgang Pauli, Proteins as Colloids; M. H. Fischer, Lyophilic Colloids and Protoplasmic Behavior; T. B. Robertson, The Combination of Proteins with Acids and Bases, with Some Observations on the Origin of Viscosity in Protein Solutions; Mona Spiegel-Adolf, Physico-Chemical Investigations on the Heat Denaturization of Proteins; G. Bredig, Inorganic Ferments; R. K. Cannan, Enzyme Reaction in Relation to Surface Catalysts; R. Willstätter, The Adsorption of Enzymes; Andor Fodor, The Present Status attained by Colloid-Chemical Investigation of Peptide-Splitting Enzymes; E. N. Harvey, Luciferin and Luciferase, the Luminescent Substances of Light-Giving Animals; William Seifriz, The Physical Properties of Protoplasm; L. V. Heilbrum, Protoplasm; R. S. Lillie, The Colloidal Structure of Protoplasm and Protoplasmic Action; Robert Chambers, The Nature of the Living Cell as revealed by Micromanipulation; Leo Loeb, Amoeboid Movement and Agglutination in Amoebocycles of Limulus and the Relation of these Processes to Phagocytosis, Tissue Formation, and Thrombosis; L. B. Wilson, The Physical Basis of Life; C. E. Simon, The Filterable Viruses; F. d'Herelle, Bacteriophage, a Living Colloidal Micell; I. S. Falk, The Colloidal Behavior of Bacteria; E. I. Fulmer, Colloids and the Growth of Microorganisms; E. E. Just, Cortical Reactions and Attendant Physico-Chemical Changes in Ova following Insemination; D. T. MacDougal, The Arrangement and Action of the Colloids of the Plant Cell; F. E. Lloyd, Colloidal Aspects of Botany; Rudolph Höber, Colloidal State and Physiological Function; H. Schade, Colloid Chemistry and Internal Medicine; Edward Zunz, The Modifications of the Dynamic Surface Tension of Plasma and Serum; Auguste Lumière, The Colloidal State in Living Organisms; S. DeW. Ludlum and A. E. Taft, Similarities in Colloidal Reactions of Blood, Simple Colloidal Solutions, and Protoplasm; H. A. Abramson, The Mechanism of the Acute Inflammatory Process; F. P. Underhill, Changes in Blood Concentration and their Significance in the Systematic Treatment of Cases of Extensive Superficial Burns; I. S. Falk, Electrophoresis of Bacteria and other Microorganisms and some Relations to Immunological Theory; L. Reiner, Colloid Chemical Problems of Serology; R. L. Kahn, Serum Diagnosis of Syphilis; P. Lecomte du Noüy, Some Physico-Chemical Characteristics of Immune Serum; J. G. M. Bullowa, Lobar Pneumonia and its Treatment with Refined Sera; H. Schade, Concretions; Leonard Greenburg, Dust, Fumes, and Smoke, and their Relation to Health; Albert Mary, Colloid Chemistry and Tuberculosis; N. Waterman, Colloid Chemistry and Malignant Tumor; A. Kotzareff, Cancer, Selective Fixation, Curiegraphy, and Organoradiumgraphy; Waro Nakahara, The Filterable Entity transmitting Chicken Sarcoma; N. Waterman, Some Therapeutic Measures founded upon the Colloid Theory of Malignant Tumor; F. V. von Hahn, Colloidobiological Study of the Vitamines; J. U. Lloyd, Colloids in Pharmacy; Hans Handovsky, The Significance of Colloid Chemistry for Pharmacology and Therapeutics; H. M. Spencer, Colloidality of Arsphenamine and its Derivatives; W. Kopaczewski, The Pharmacodynamics of Colloids.

In the first paper Alexander and Bridges explain life by postulating that the genes are reproductive catalysts, which seems to be juggling with words. "The facts of linkage have led to the conception of the gene as a definitely delimited, definitely localized sub-unit in the structure of the core, or gene-string, of the chromosome. To this must be added the view that each gene is a definitely organized self-reproductive unit. With each cell generation, the original gene gives rise to two daughter genes identically located and with the identical characteristics of the parental gene, as judged by the identity of effects in successive generations. In the increase in the amount of the substance of the particular gene, preparatory to division, constituents that were present in the surrounding medium interact or condense to produce a specific end-product. In the case of contiguous but unlike genes, the raw materials present in the surrounding medium are essentially the same. The primary difference between the two types of synthesis, carried on simultaneously and in close juxtaposition in the cell, must be sought, not in the cell plasma at large, but in the particular definite locus in which each synthesis occurs and continually reoccurs. Effective synthesis of each particular type is restricted to a particular locus, and hence must depend upon the action of some materials situated at that particular locus. But when this synthesis has occurred, the substance has not been used up, or else it has been reconstituted, for in the daughter loci the same reaction is repeated at the succeeding growth period. This suggests that the condensation is catalytic, and specifically catalytic, since in adjacent loci different condensations occur. The situation can be accounted for on the assumption that the specific catalyst is the genic material itself. . . .

"If, as seems certain, the genic molecules act also as heterocatalytic enzymes, other specific end-products of greater variety are synthesized. Considered from the stand-point of the end-products, genes are chemical factories, each of which is synthesizing a characteristic set of end-products which are delivered ultimately to the common cytoplasm. The various products influence the constitution of the nucleoplasm and of the cytoplasm directly by being constituent parts, and indirectly by their interactions with one another and with the host of materials diffusing in from the milieu of the cell. Also the products of one gene may act as the raw materials for the syntheses carried out by other genes. In producing and controlling development, the genes of the entire complement act together, since all are liberating their chemical products into the common cell plasma. But since the products of the different genes are different, they take effect in different ways upon the developing organism. Some of the genes will have much effect upon one character and only slight effect upon another. Each character will be determined by all the genes, but in each case most of the effect will be produced by a relatively small proportion. For example, in Drosophila the products of one gene are predominantly concerned with eye-color, but have accessory effects upon the wings, while the products of another gene influence greatly the number of bristles, but have also slight effects upon a dozen other characteristics," p. 46.

"Bottazzi draws the following conclusions in regard to the influence that certain protein substances, alkaloids, soaps, etc., exert upon the surface tension of water, p. 162. "These substances are capillarily active only when existing in a state of true solution, while they are inactive when found dispersed as submicrons (or colloidal). Hydrolysis (submicronic dispersion) causes a surface tension somewhat lower than that of the pure dispersion medium; but this probably depends upon the fact that the system contains a part of the substance, even though little, as dispersed or dissolved molecules. Of the soluble substances the undissociated molecules—not the ions—are responsible for *lowering the surface tension*. The minimum lowering of surface tension of a protein solution always corresponds to the isoelectric point of the dissolved protein. That is to say, we have a means of determining the isoelectric point of a soluble protein by measuring the surface tension of its solutions

"Undissociated molecules of a protein, of an alkaloid, of a soap, etc., are generally less hydrated than their ions. They have a greater tendency to aggregate into submicrons. When one reduces the electrolytic dissociation of a salt of a protein, of an alkaloid, or of a fatty acid, etc., the process of association does not stop at the formation of undissociated molecules, but proceeds further to the formation of molecular aggregates; that is, of submicrons and of microns. Simultaneously, the surface tension of the liquid is lowered;

but the lowering of the surface tension is not due to their formation. It is due instead to the formation of undissociated, free molecules of protein, of alkaloid, of fatty acid, etc., which remain invisible in the ultra-microscope."

Robertson starts his paper, p. 255, with the unfortunate statement that "it is now admitted by all observers who have directed adequate attention to this question, that the proteins accomplish the neutralization of acids and bases in stoichiometrical, that is molecular or equivalent molecular proportions." The catch is in the word "adequate."

Robertson does admit, however, that the acid-combining powers of some proteins are not due to free amino groups, p. 258. With edestin the acid-combining power corresponds to nine amino groups per molecule or something over ten percent of the total nitrogen. "Since only 1.8 percent of the total nitrogen of the edestin molecule is actually present therein in the form of amino groups, no less than eighty percent of the neutralizing power of edestin for acids must be accounted for in some other fashion than by the assumption of a union of the acid with free amino groups. . . . At least half the capacity of casein to neutralize acids is attributable to elements in the molecule other than amino groups. . . . Even if we adopt Hitchcock's estimate of the combining weight of gelatin [1120] instead of Procter and Wilson's smaller figure [768], the amino groups required would still be twice as many as gelatin actually contains.

"The protamin, salmin, unites with sulfuric acid to form a compound of the composition $C_{30}H_{57}N_{17}O_6.2H_2SO_4$, yet salmin yields no nitrogen on treatment with nitrous acid, because it contains no lysine. Sturin contains 67 percent of its nitrogen in the form of arginine, 10 percent in the form of histidine, and 6 to 7 percent in the form of lysine. It yields nitrogen on treatment with nitrous acid corresponding to the ω-amino group of the lysine. Only about three of every hundred nitrogen atoms in sturin are therefore present in the form of free amino groups. Yet one hundred nitrogen atoms in sturin will neutralize no less than 24 equivalents of acid. Evidently at least twenty of these acid molecules must attach themselves to the molecule of protein at some other points than those provided by amino groups."

Robertson quotes Bugarszky and Liebermann, p. 279, to the effect that hydrogen and chlorine ions disappear to a very considerable extent on adding hydrochloric acid to albumin. "At least 97 percent of the hydrochloric acid is bound by the egg-albumin. The observed 'molecular' conductivity (67×10^{-3}) is at least seven times greater than could be accounted for by the maximum possible residuum of unneutralized hydrochloric acid and must therefore have been due to the protein-acid compound. We are therefore impelled to conclude that the compounds of proteins with acids and alkalis are ionized in aqueous solutions; but that, in many cases, for instance the caseinates and serum globulinates of the alkalis and alkaline earths, and the compound of egg-albumin or of albumose with hydrochloric acid, the inorganic ion is not dissociated as such. The ions which are actually present in these solutions must therefore be protein ions, a proportion of which carry the inorganic radical bound in a non-dissociable form," p. 283.

Cannan says, p. 354, that "the adsorption theory does, as we have seen, permit a useful interpretation of the main catalytic activities of enzymes; and modern views of the nature of adsorption go far towards reconciling the physical theory with our natural prejudice for finding a chemical explanation for catalytic processes which appear on their face to be chemical phenomena."

Seifriz points out, p. 407, that "Warburg and Meyerhof observed enormous increases in the oxygen consumption of an egg at the time of fertilization. The Needhams found that there is no change in internal pH at the time of fertilization of echinoderm and tunicate eggs; nor is there any change in rH on fertilization. These data are most striking in the face of the findings of Warburg and Meyerhof which reveal a 200-fold increase in oxidation at fertilization. The data support Warburg's earlier statement that rate of oxidation is independent of the oxygen pressure, i.e., of the oxygen concentration in the egg."

Chambers says, p. 486, that "the variation between the behavior of eggs immersed in potassium chloride and those in their normal environment of sea water containing calcium may be accounted for as follows. The protoplasmic surface of the echinoderm egg is coated with a thin layer of glutinous jelly, secreted by the egg. This is the pellicle which, as mentioned in the earlier part of this lecture, is more or less universally present on living cells. Any newly formed surface, e.g., the sides of the cleavage furrow, exudes a substance which, in the presence of its normal calcium-containing environment, immediately sets to form a jelly. In the absence of the bivalent cations, calcium and magnesium, the material either dissolves or is softened and washed away. In a solution of potassium chloride, therefore, the egg can divide only when the opposite sides of the furrow do not come in contact. Otherwise, there is nothing to prevent their merging with the consequence that the furrow disappears. In normal sea water, on the other hand, the furrow fills with a jelly as fast as it sinks into the egg. The jelly separates the protoplasmic surfaces bordering the furrow, and prevents their mergence, thus enabling the cell to divide. This phenomenon lines up with our knowledge concerning the need of calcium for the growth of tissues in general. We can now see that, in the growth process, one of the requirements which is filled by calcium is to stiffen the intercellular substance. This increases the chances of cell division and also enables the cells to adhere so as to form a coherent tissue."

While discussing the physical basis of life, p. 523, E. B. Wilson says: "What then constitutes the organization of the egg? No one has yet found an adequate reply. The embryologist, the cytologist, the physiologist, and the biochemist, all of these alike have thus far only skirted the outermost rim of the problem. We cannot predict how far the cytologist of the future may be able to penetrate into it; but it would seem that, sooner or later, his way will finally be blocked by inherent limitations of the microscope determined by the wave-length of light. If we are ever to find our way into the innermost arcanum of the cell, other methods must be employed; and we must marshal and coördinate all the resources of experimental embryology, genetics, biophysics and biochemistry. Many important discoveries in these various fields have in recent years advanced our knowledge of development; bu they leave its central problem still unsolved."

MacDougal says, p. 568, that "by measurements of the reactions of roots of lupine to neutral salts in hypotonic solutions, Kahho confirms the series as to permeability of cations which runs $K > Na > Li > Mg > Ba > Ca$, in which the greatest penetrability is shown by potassium and the least by calcium. It is also seen that the interferences are such that each cation is retarded by those to its right, and that the greatest retardation is by the cations which show the greatest coagulating action on colloids. The cations which have the least *coagulating action on colloids* penetrate most rapidly. The anions retard the colloidal or coagulative action of the cations in a series, citrate < sulfate < tartrate $< Cl < NO_3 < Br < I$, in which the effect is least with the citrate and most with the iodine. That is, each cation has the greatest effect when combined with the citrate and least with the iodine. As a further consequence, the citrates have the least penetrability and the salts of iodine the greatest."

Schade says, p. 633: "Even today, though colloid science has had but a decade and a half of development, there is unmistakably a revolutionary change of view in wide medical circles. Striking new results of far-reaching significance have led a not inconsiderable number of physicians to believe that in colloid research lies the key to profound penetration of the mysteries of etiology. Colloid chemistry has discovered the laws of the peculiar behavior of matter in microheterogeneous dispersion. Everywhere in the body, in cells, in intercellular tissue, in blood, and in the body fluids are found colloids, some as sols of fluid nature, some as gels; practically every process bears the imprint of their individuality. Just for this reason in many cases which were previously incomprehensible to physics and chemistry, colloid chemistry was the magic wand to effect a solution. It was furthermore established that in practically every occurrence in the human body, it is indispensable to consider colloid chemistry, which has thus become a fundamental factor in etiology. The vivification of medicine by colloid chemistry justifies us in calling this the beginning of a new era in etiology."

Greenburg points out, p. 855, that "it is an interesting and significant fact that in every instance, as far as we are aware, in which a heavy incidence of tuberculosis has been shown to result from exposure to industrial dust, the dust in question has been in part at least made up of crystalline rock. It is silicosis which lies at the basis of miners' phthisis, and silicosis is probably the chief disposing factor in tuberculosis among axe grinders, although in grinding and polishing, steel dust may, and probably does, play a part as well."

The death rate from tuberculosis among axe grinders and polishers is 1900 per 100,000 as against a normal rate of about 160. This is an additional argument in favor of alundum and silicon carbide grinding wheels.

On p. 925 von Hahn says: "The so-called vitamin-containing substances act by virtue of their inherent surface activity and not by means of a chemical constituent in them. . . . We must submit proof that actual surface—active substances can serve substitutes for vitamines. . . . The first case is that of a 34-year-old shoemaker, who, for about three and one-half years, had been nourished exclusively on bread, meat and conserves. During this time he had had no illness and had not lost weight. Suddenly he awoke one morning with a severe stomatitis and greatly dilated blood vessels in the subcutaneous connective tissue of the extremities. At first there appeared to be no etiologic moment for the outbreak of the scurvy. After exhaustive questioning, the following interesting history was obtained. Three days before the patient's illness, his landlady was taken sick and removed to the hospital; the only resultant change in the patient's manner of living was that he was no longer able to obtain his usual morning coffee. According to his statement, he drank two to three cups of strong bean coffee early every day. We do not assert that the strongly active coffee had supplied the surface activity necessary for unlimited resorption during the three and one-half years of a diet without vitamin, i.e., surface-active foods. This substitution could have been sufficient only in an emergency. In other words, the malcompensation of the resorption disturbed by faulty nutrition, was balanced by the coffee; the condition must therefore afterward have become evident immediately, when this last saving agent for resorption failed."

Handovsky says, p. 948: "In his analysis of the Ca-cocaine antagonism, A. Mayer points out that cocaine inhibits blood clotting (Zak); that its anesthetic action is inhibited by lecithin because it is bound by lecithin (Storm van Leeuwen), and finally that a precipitation of a lecithin emulsion by Ca is inhibited by cocaine. Mayer concludes that calcium and cocaine displace each other in the combination with lecithin and that their functional antagonism is related to this fact."

There is no unity in the volume because the editor does not believe in that. It may be helpful to have such contradictions as occur in the papers on protoplasm, for instance; but a critical discussion will be necessary some day and why not now? Many of the papers are very bad and are of value only in showing what the authors do not know about colloid chemistry. That brings the value of the book down to the values of the occasional facts that one may find scattered through the book. The reviewer has profited by his reading of the volume; most people will not. In an appendix is given Jacques Loeb's Pasteur Lecture delivered in 1922. It is a little brutal to reprint, p. 991, the sentence: "We therefore come to the conclusion that the chemistry of proteins does not differ from the chemistry of crystalloids, and that proteins combine stoichiometrically with acids and alkalis, forming protein salts which dissociate electrolytically."

Wilder D. Bancroft

Physikalische Chemie der Silikate. *By Wilhelm Eitel. 24 × 17 cm; pp. xi + 552. Leipzig: Leopold Voss, 1929. Price: 60 marks; bound, 63 marks.* This book aims to do more than its title says, and to include the physical chemistry of the silicate industries. The book is divided into six parts: states of aggregation of the silicates, with chapters on the crystalline state, the fused and glassy states, and the colloid state; thermochemistry of the silicates; equilibrium conditions for dry silicates; special silicate systems; systems composed of silicates and volatile substances; technical silicate systems, with chapters on technical glasses and slags, ceramic bodies, cements and mortars.

According to Washington, p. 8, the percentages of silica in the different zones of the earth are: granite layer, 59; basalt layer, 48; periodotite zone 44; ferrospore zone, 35;

lithospore zone, 18; nickel-iron center, none. It seems probable that there are acid silicate rocks on the moon because of the high albedo.

Niggli, p. 51, has made a model of the magnetic silicates with mercuric iodide and bromide for the silicates and sulphur dioxide for water. He has also suggested substituting carbonates for silicates. Goldschmidt finds that the crystal structure of barytes can be duplicated with rubidium borofluoride, and of magnesia with lithium fluoride.

According to Samsoen and others, there is always a curious break in the temperature-specific heat curve when a liquid changes to a glass, p. 106. An account is given, p. 109, of the view of Parks that a glass is different from a supercooled liquid. On p. 118 there is a brief discussion of glasses other than silicate ones.

The author seems to adopt the view that no compounds of alumina and silica are formed by wet precipitation, p. 141. He does not discuss the question as to the stage at which compounds disappear in the weathering of the feldspars. The silica seems to be the part of the clay which adsorbs dyes the most strongly, p. 146; but the alumina in kaolin seems to determine the catalytic decomposition of alcohol. The adsorption of cupric ions by kaolin passes through a maximum with increasing concentration, p. 147.

Under colloid-chemical theory of glasses is the view that the increasing viscosity of cooling glass melts is due to the formation of silica chains or complexes, p. 150, just as we get filaments formed in soap solutions. Berger considers that what he calls the aggregation temperature, p. 152, can be determined with a fair degree of accuracy. For fused silica this is about 1000°; for sodium silicates the value is nearer 900°, p. 153. Fulcher has even written equations for the relation between the viscosity and the temperature, and has calculated the aggregation temperature from his equation.

There is a good diagram, p. 190, to show the qualitative relation between temperature and rate of crystallization, formation of nuclei and tendency to crystallize (Tammann). It is recognized, p. 191, that the blue color of Jena-glass combustion tubes is a structural color, produced by crystallization.

There is a good discussion of mullite and sillimanite, pp. 297-300. Presence of iron and titania in mullite may change the index of refraction enough to make it impossible to differentiate mullite and sillimanite by the optical method.

Manganous oxide and silica seem to form from the melt the compounds Mn_2SiO_4, $Mn_3Si_2O_7$, and $MnSiO_3$, p. 310. With ferrous oxide and silica, we get Fe_2SiO_4, $FeSiO_3$, each stable at its melting-point, p. 311. Formulas are written on p. 352 for white, green, and blue ultramarine; but it is not maintained that they are right. The author implies, p. 311, that Hofmann and Resenscheck discovered Prussian blue; but of course does not mean that.

At 500° the rates of diffusion of helium and hydrogen through quartz glass are as 122:1 although the solubilities of the two gases are approximately the same, p. 361. The author seems to think that is a question of holes, p. 363, because the diameter of the helium atom is 19×10^{-9} cm, while the diameter of the hydrogen molecule is 23×10^{-9}; but his explanation will not appeal to most people.

When the amount of water in heulandite gets below three mols, the process becomes irreversible; but we have reversible addition and removal of water for values exceeding three mols, p. 413.

On p. 464 there is a discussion of white enamels and on p. 484 a discussion of plasticity of clay. The author does not lay the stress that he should on the necessity for a gelatinous film. On p. 488 is expressed the opinion, without reference to Mellor, that the change on heating kaolin to 600° is a loss of water and a separation of the adsorption complex into alumina and silica, without giving any adequate proof for this view.

H. George found, p. 502, that addition of water to fused silica gave a denser quartz glass. This is ascribed to the gas reaction,

$$Si + H_2O \rightleftharpoons SiO_2 + H_2$$

The author accepts Rayleigh's suggestion for quartz glass from sand being turbid, that gas bubbles are evolved from the sand grains on fusing.

The book is an interesting one and contains much valuable material. The author is more appreciative of American work than is sometimes the case. A good deal of space could have been saved, if, the author has been able to assume that his readers knew something about the phase rule. It is a pity to have to repeat so much that is elementary, and that the reader should have had in some earlier stage of his education.

Wilder D. Bancroft

Catalytic Processes in Applied Chemistry. *By T. P. Hilditch. 22 × 14 cm; pp. xx + 360. London: Chapman and Hall, 1929. Price: 16 shillings.* That branch of applied physical chemistry which is comprehended under the heading of catalysis is rapidly coming into prominence in industry. Whereas at the beginning of this century, apart from the contact process for making sulphuric acid, there was but little application of catalysts; its early years saw first the invention of the nickel process for the hydrogenation of fats and then the synthesis of ammonia from the nitrogen of the air followed by its oxidation in presence of platinum or of an iron-bismuth oxide catalyst to nitric acid. Such methods today are at the basis of chemical industry and they are being followed on the large scale by a series of organic synthesis in presence of catalysts which are likely to have a far-reaching consequence. The opportunity for a book correlating principles with practice in this field is considerable whilst Professor Hilditch is especially qualified to undertake the task since, after a lengthy scientific training, he distinguished himself in the practical application of catalytic principles and has now returned to academic ranks. The scope of the book is a simple one: it is divided into four sections dealing in sequence with the general principles of catalytic action, with catalysis at the surface of solid inorganic materials, with catalysis at the surfaces of colloidal organic materials which brings it into the realm of fermentation processes and lastly with homogeneous catalysis in liquid systems.

The author has, wisely in our opinion, refrained from trying to cover too wide a field: in order to make the work appeal to the largest possible public he has eliminated mathematical treatment on the one hand and illustrations and drawings of plant on the other neither of which are helpful to the ordinary reader. For the same reason the book is not overburdened with references to the original literature but contains at the end of each chapter a brief bibliography of papers which may be consulted with advantage and will themselves put the earnest student on the track of further work.

Perhaps many readers will be astonished at the extent to which catalytic processes are penetrating into chemical industry and displacing the older methods, for example the production of anthraquinone derivatives via phthalic acid from naphthalene by means of air oxidation in presence of vanadium is making the isolation of anthracene from coal tar superfluous. But the applications of catalysis today are only a tithe of what may be expected during the next decade and in the reviewer's opinion it will be well worth the while of the teachers of those about to enter chemical industry to equip them with a complete and critical knowledge in this field. The book under notice should serve admirably for this purpose; indeed we regard it as the best book of its type which has come into our hands during a number of years.

E. F. Armstrong

Polarisation diélectrique. *By J. Errera. Recueil des Conférences-Rapports de Documentation sur la Physique. Vol. XV. 25 × 16 cm; pp. 172. Paris: Les Presses Universitaires de France, 1928. Price: 35 francs.* The scope of this valuable little work is indicated by its sub-title: "Refraction des Radiations depuis les Rayons X jusqu'aux Ondes Hertziennes"; and it covers admirably in outline the ground thus indicated. An introductory chapter dealing generally with electromagnetic waves, the structure of matter and the relationship of the waves with matter, gives in very small compass an interesting and accurate outline of the relevant facts and theories. This is followed by some forty pages on the theoretical aspects of the study of refraction, including such topics as the formation of the secondary wave in matter as a result of the incidence of the primary wave, the refraction of polarisation of low-frequency waves and the general mathematical theory of polarisation.

The largest section of the book, eighty pages, discusses the experimental study of refraction and polarisation of non-ionised pure substances, and this is followed by a separate chapter dealing with refraction in systems such as colloidal solutions, solutions of polar molecules in neutral solvents and ordinary solutions of electrolytes. There is a final short chapter on refraction in metals. The book is well documented and the chapters on the experimental data are liberally illustrated by tables and graphs.

It is, perhaps, necessary to warn the reader that the book is not intended to be a guide to experimentation in its field. The experimental chapters certainly give outlines of some typical methods, but they are chiefly concerned with the experimental data and their theoretical interpretation and many experimental methods of practical value are necessarily omitted without even a reference. From one point of view this is unfortunate because in some cases, for example in the matter of determining dielectric constants, this treatment may leave the reader without an adequate appreciation of the experimental difficulties and hence with a respect for the precision of the published data which they scarcely merit. It is hardly fair, however, thus to criticise such omissions when it is evident that to rectify them would have involved a fundamental change in the whole conception of the work and would have changed it from a compact theoretical monograph to a bulky, practical "Handbuch."

The author is to be congratulated on producing a book which will be extremely useful to anyone who desires a general conspectus of the facts and theories relevant to the refraction and dispersion of electro magnetic waves of all kinds, and especially of the conclusions which may be drawn from the experimental observations with regard to polarisation, whether due to electronic or atomic shift within the molecules owing to the incidence of radiation or to permanent dipole structure.

H. V. A. Briscoe

Photometric Chemical Analysis. *Volume II. Nephelometry. By John H. Yoe. With contributions by Hans Kleinmann. 23 × 15 cm; pp. xvi + 337. New York: John Wiley and Sons, 1929. Price: $4.50.* This book has been written for advanced students in chemistry and for research workers in biological, medical, pharmaceutical, and industrial chemistry, with the six-fold purpose: (1) of giving an accurate account of the development of nephelometry, (2) of presenting an impartial discussion of the present status of the theory of nephelometry, (3) of giving detailed working-directions for using a precision nephelometer, (4) of discussing nephelometric research, (5) of giving procedures for the determination of a number of inorganic and organic constituents, and (6) of giving an accurate and fairly complete survey of the literature on nephelometry.

The author is to be commended upon the excellent manner in which he has fulfilled his purpose giving to all, whether novices or experienced workers in this field, a clear insight into the technic, precautions, speed, and accuracy to be expected of this method of analysis. As a result of this treatise nephelometry will undoubtedly come into more general use both in routine analytical work and in research problems.

The author hopes that this book "will prove useful not only as an aid in the various fields of applied chemistry but also in stimulating research in developing new nephelometric methods of analysis" and in the opinion of the reviewer this second volume fulfills all the desires of the author. It is recommended, together with the first volume on colorimetry, as an extremely valuable adjunct to the library of anyone, who may have occasion to use these methods of analysis.

M. L. Nichols

Erratum

In the paper by Messrs. Haring and Vanden Bosche: J. Phys. Chem., 33, 165 (1929), the E_h values for nickel, given by Glasstone and Shildbach, were quoted erroneously as −0.288 and −0.198 volts. They should be −0.57 and −0.253 volts respectively.

THE POLYMORPHISM OF SODIUM SULFATE:

I. THERMAL ANALYSIS

BY F. C. KRACEK

Introduction

Altho the study of inversions or transitions in crystals has occupied the attention of chemists and crystallographers for at least a hundred years, particularly during the last twenty years of the preceding and the first decade of this century, it must be admitted that our knowledge of these phenomena is still largely incomplete. This is forcibly borne out by the extensive work of E. Cohen[1] and co-workers, among others.

Inversions proceed with a great variety of speeds, varying from the extremely sluggish transitions characteristic of the principal forms of silica (quartz-tridymite-cristobalite) to the very rapid ones such as high ⇄ low quartz or the rapid enantiomorphic transformations in many salts, e.g., KNO_3, $AgNO_3$, K_2SO_4. These are called high-low inversions by Sosman.[2] The sluggish and high-low inversions, however, are the extreme cases, and a very great number of polymorphic changes proceed at moderate speeds in both directions. Some enantiomorphic inversions are pseudo-monotropic, that is, while reversible under certain conditions, they ordinarily proceed with measurable speed in one direction only, usually at a temperature much above the point of thermodynamic equilibrium. The calcite-aragonite inversion appears to be of this type. Another example is found in the behavior of anhydrous sodium acetate. Some of the phenomena described in this paper fall into this class.

It has long been known that anhydrous sodium sulfate inverts in the neighborhood of 234°. While engaged in the recalculation of the vapor pressure and solubility data for the system $H_2O—Na_2SO_4$[3] I had my attention drawn to apparent discrepancies in the published statements with regard to this inversion.[4] The results of optical studies and of thermal analysis are not in agreement. The temperature 234° quoted above is based on the principal arrest obtained with cooling curves, and represents, as will be seen later, only one of several arrests occurring in heating and cooling curves made on preparations of known thermal history. Optical examination also reveals the existence of several forms. A brief recapitulation of published optical studies on this substance is given in Table I.

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[1] E. Cohen: "Physico-chemical Metamorphosis and Problems in Piezochemistry," (1926).

[2] R. B. Sosman: "The Properties of Silica," pp. 41-179 (1927).

[3] F. C. Kracek: P-T-X relations for systems of two or more components and containing two or more phases (L-V, LI-LII-V and S-L-V systems). Int. Crit. Tables, 3, 371 (1927).

[4] Most of the pertinent references are given by H. W. Foote: Int. Crit. Tables, 4, 7 (1928), who estimates the temperature of the inversion to be 236 ± 3°. An error is found in Int. Crit. Tables, 1, 150, where it is stated that thenardite changes at 100° to a monoclinic form which then changes at 500° to hexagonal. No basis has been found for these values.

TABLE I

Characteristic Observations on Polymorphism of Na_2SO_4

1. Mügge: Neues Jahrb. Mineral. Geol., **1884** (2), 1-14; microscopic examination of preparations after heating to various temperatures. Optical properties of thenardite are permanently altered, the birefringence being markedly decreased to a low value, by heating. Beginning of change 185°-205°, end of change 215°-225°, in some cases not till 240°. Always completely changed at 260°; no further permanent change by heating to 330° and higher. Temperature of beginning of alteration variable for different fragments of same crystal as well as for different crystals. Fragments do not alter completely at one temperature after change starts. Hot slide placed quickly under the microscope with nicols crossed shows on cooling a momentary intensification of birefringence accompanied by violent motion of the particles; the same phenomenon is exhibited by slides prepared from molten Na_2SO_4. In both cases the final form is that characteristic of altered thenardite.

2. Wyrouboff: Bull. Soc. min. France, **13**, 311-6 (1890); optical examination with a heating microscope. Na_2SO_4 exists in 4 forms:
    - α, ordinary thenardite, orthorhombic, moderate birefringence, stable to 200°.
    - β, probably monoclinic and analogous to ordinary Li_2SO_4. High birefringence. Stable above 200° and below 230°; can be cooled to room temperature. Always mixed with other forms.
    - γ, orthorhombic, analogous to K_2SO_4. Low birefringence, optically negative. Very stable when cooled to ordinary temperature. Density 2.696.
    - δ, hexagonal, isomorphous with high-temperature form of K_2SO_4, low birefringence. Stable only at high temperature.*

    Transformation is indirect and sluggish for the first three forms; rapid and easily reversible for the last two.

3. Nacken: Neues Jahrb. Mineral. Geol. Abt. A, Beil. **24**, 27-9, (1907). Optical examination with heating microscope. A gradual decrease in birefringence on heating toward 230°. Irreversible. Further heating to near melting produces no other sudden change in optical properties.

4. Müller: Neues Jahrb. Mineral. Geol. Abt. A, Beil., **30**, 33-5, (1910). "Na_2SO_4 is orthorhombic when crystallized from solution, and 'pseudohexagonal' at ordinary temperature when crystallized from melt. High temperature form is hexagonal, isomorphous with the hexagonal $4Na_2SO_4 . CaSO_4$." The irreversible transformations observed by others assumed to be incorrect.

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* Wyrouboff estimated the corresponding inversion temperature as 500°. Jaenecke (Z. physik. Chem., **91**, 548 (1916)) recorded an indefinite heat effect at 400 ± 50°, which he later retracted (Z. physik. Chem., **91**, 676 (1916)).

Correlation of the statements in Table I indicates that the behavior of Na_2SO_4 is far from simple. The existence of three modifications is certain, namely: (a) thenardite, which separates above 32.5°C from aqueous solutions saturated at atmospheric pressure; (b) the low birefracting form which appears when Na_2SO_4 heated to high temperature is cooled down to room temperature; and (c) the hexagonal high-temperature form. The existence of two other forms is probable. Wyrouboff observed a modification of higher birefringence than thenardite, which he called the β modification, and which he would keep at room temperature for some time. This β form results from thenardite and changes on further heating into his γ modification considered above under (b). It is reported to be always admixed with thenardite (α) and the γ modification. Careful microscopic work is required to detect the β form, as it is never present in very large amount. Mügge, on the other hand, noticed that Na_2SO_4 cooled from high temperature under the microscope passes momentarily thru a phase which is more birefringent than either the high-temperature hexagonal δ form or the (metastable) γ form of Wyrouboff which is the inert modification resulting from cooling to room temperature. This Mügge modification, according to our experience, can be obtained and preserved for only a short time by quenching from above 260°.

Smits and Wuite's[1] work on the vapor pressures and solubilities of saturated aqueous solutions of Na_2SO_4 yields a definite break at 235° with an uncertainty of about 5°. The small number of points established by them and the low accuracy obtainable in this difficult region do not warrant conclusions about the course of the curve below this break.

In connection with the consideration of the complex behavior of Na_2SO_4 it is of interest to note that the anomalies were recognized, from studies on the heats of solution of the salt, several years before its polymorphism was established. Berthelot[2] and Thomsen[3] differed on the heat of solution by amounts considerably in excess of the probable error of their determinations; moreover, they found some difficulty in reproducing their own values, dependent upon the thermal treatment of the salt before dissolving. Pickering[4] took up the question in the same year that Mügge published the results of his optical study; he found that the heat of solution of 1 mol of Na_2SO_4 in 420 mols H_2O was about 60 cal. for salt dried at a temperature not exceeding 150°; if the salt was dried considerably above 200°, but below the melting point (884°) he obtained an average value of 760 cal., or an apparent discrepancy of 700 cal. for the two heat treatments. This is quite in order, in view of the optical results which clearly show that previously ignited Na_2SO_4 differs from thenardite.

No detailed thermal analysis of the inversions in Na_2SO_4 exists to date and no heating curves appear to have been published. The latter are greatly

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[1] Smits and Wuite: Versl. kon. Akad. Amsterdam, Sept. (1909); Wuite: Z. physik. Chem., **86**, 349 (1914).

[2] Berthelot: Ann. Chim. Phys., **14**, 445 (1878); **29**, 295 (1883).

[3] J. Thomsen: J. prakt. Chem., **17**, 171 (1878); **18**, 5 (1878).

[4] Pickering: J. Chem. Soc., **45**, 686 (1884).

needed in order to confirm and extend the optical results, which indicated that the heating and cooling curves should show quite different characteristics. This expectation has been completely verified; indeed the complexity of behavior exceeds that of any single system hitherto investigated in detail if we exclude the behavior of silica and analogous substances, in which the complexity is of a totally different character. According to the present data, Na_2SO_4 exhibits pentamorphism within the comparatively narrow temperature range from *ca.* 190° to 250°, accompanied by pseudo-monotropic behavior of some of the inversions. Precedent for this type of behavior is not definitely established; it may, however, be of interest to direct attention to the work of Bowen and Greig[1] on carnegieite in which anomalous heating curves were also encountered.

This paper forms the initial communication of a series in which it is proposed to investigate the nature of the polymorphism exhibited by this substance as completely as is possible with the methods at our disposal.

Experimental Part

1. *Materials.* The sodium sulfate used in this work was prepared in the form of thenardite, by purification and recrystallization in various ways, from Baker's "Analyzed" or Kahlbaum's Anhydrous Na_2SO_4. The purchased salt was dissolved in water and filtered free of mechanical impurities and of the precipitate due to small amounts of Fe and Al present. No other impurities were found in detectable amounts. The clear solution of pure Na_2SO_4 was then crystallized by evaporation above 50° in open or covered vessels, or precipitated by pouring the warm solution into warm 95 per cent alcohol. In addition to these methods, samples of anhydrous Na_2SO_4 were prepared by slow dehydration of the deca- and the hepta-hydrates over KOH or H_2SO_4 in vacuum desiccators. The information on the materials used and their methods of preparation is collected in Table II.

TABLE II

Materials and their Methods of Preparation

No.	Method of preparation; condition	Loss of H_2O on ignition %
1	Solution evaporated in wide mouth flask at 70–80°. Uncovered. Crystals formed largely as crust on surface. Neutral.	0.10 (ungraded)
2	Neutral solution slowly evaporated in covered Pyrex beaker at *ca.* 70°. Beautifully formed large crystals up to 6 mm. along an edge. Crystals neutral.	0.046 (48–100 mesh) 0.028 (10–28 mesh)

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[1] Bowen and Greig: Am. J. Sci., 10, 204 (1925).

TABLE II (continued)

No.	Method of preparation; condition	Loss of H_2O on ignition %
3	Faintly acid (H_2SO_4) solution evaporated as in 2. Large clear crystals. Acidity of crystals 0.001 mols acid per mol of salt.	0.0396 (10–28 mesh)
4	Faintly alkaline (NaOH) solution evaporated as in 2. Large clear crystals. Salt almost neutral to phenolphthalein.	No loss
5	0.02 N acid (H_2SO_4) solution evaporated as in 2. Large clear crystals. Acidity of crystals 0.00400 mols acid per mol of salt.	0.019 to 0.024 (10–28 mesh)
6	Slightly unsaturated solution at 50° poured into 95% alcohol at 50°; motor stirring. Very fine crystalline powder. Crystals neutral.	<0.05
7	Same, hand stirring. Digested with solution at *ca.* 70° for 2 hrs. Coarsely crystalline powder. Crystals neutral.	<0.05
8	Slow dehydration of heptahydrate over KOH. Exceedingly fine powder. Neutral.	<0.05
9	Slow dehydration of decahydrate over KOH. Exceedingly fine powder. Neutral.	<0.05
10	Baker's Analyzed anhydrous Na_2SO_4. Neutral. Small amount of foreign matter.	0.10 (ungraded)

All samples dried below 125°.

Nearly all the preparations contained small amounts of moisture; microscopic examination discovered it as minute inclusions, lying principally along the planes of coalescence of adjoining crystals. This moisture is not completely removed by heating to 200°; in fact, there is reason to believe that some aqueous inclusions persist to a considerably higher temperature.

2. *The Experimental Arrangement.* Two to three gram samples were heated in a Pt thimble crucible alongside a neutral body in a nichrome-wound tube electric furnace at controlled rates. The temperature of the charge and the differential temperature between the charge and the neutral body were measured by means of calibrated Au-Pd vs. Pt-Rh (40% Pd, 10% Rh) thermocouples and a high-sensitivity potentiometer system,

capable of reading directly to 0.5 microvolt. At the temperatures involved these thermocouples have a sensitivity of 50 microvolts per 1° so that 0.01° changes could be easily detected; in general only whole microvolts were recorded.

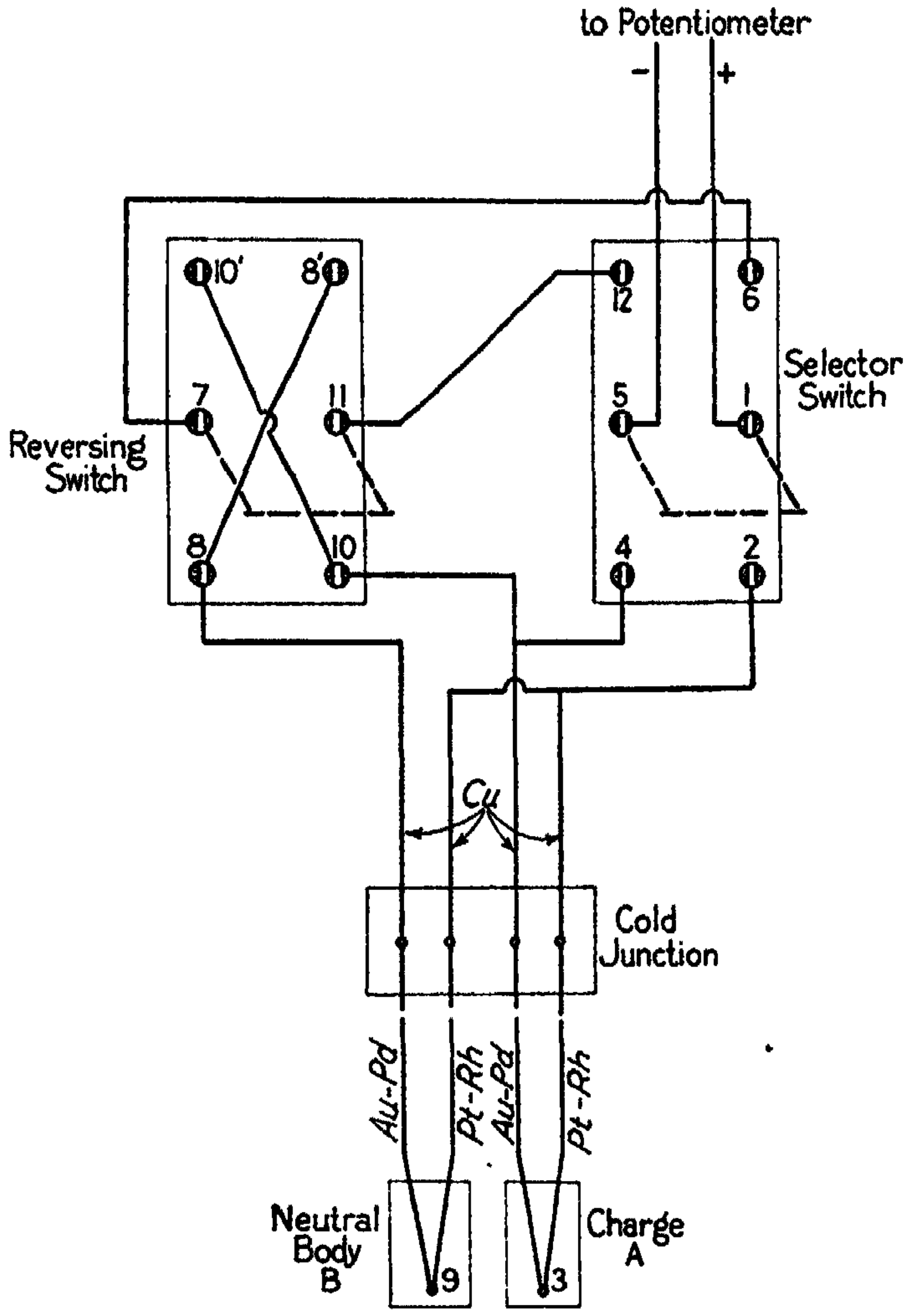

FIG. 1
Switching arrangement for thermocouples.

Two thermocouples were connected in a differential arrangement as shown in Fig. 1, one placed in the sample, the other in a neutral body of alundum cement which shows no heat effects in the region under investigation. The selector switch connects the potentiometer either with the thermocouple reading the temperature of the charge, or with the two thermocouples opposed to give the differential temperature. The reversing switch controls the direction of the differential e.m.f., making it possible to balance the differential on the potentiometer in the usual way, whether the charge or the neutral body is warmer. This switch is particularly useful when the direction of the differential changes during the course of a run. All essential parts of the switching arrangement are of copper to guard against stray electromotive forces.

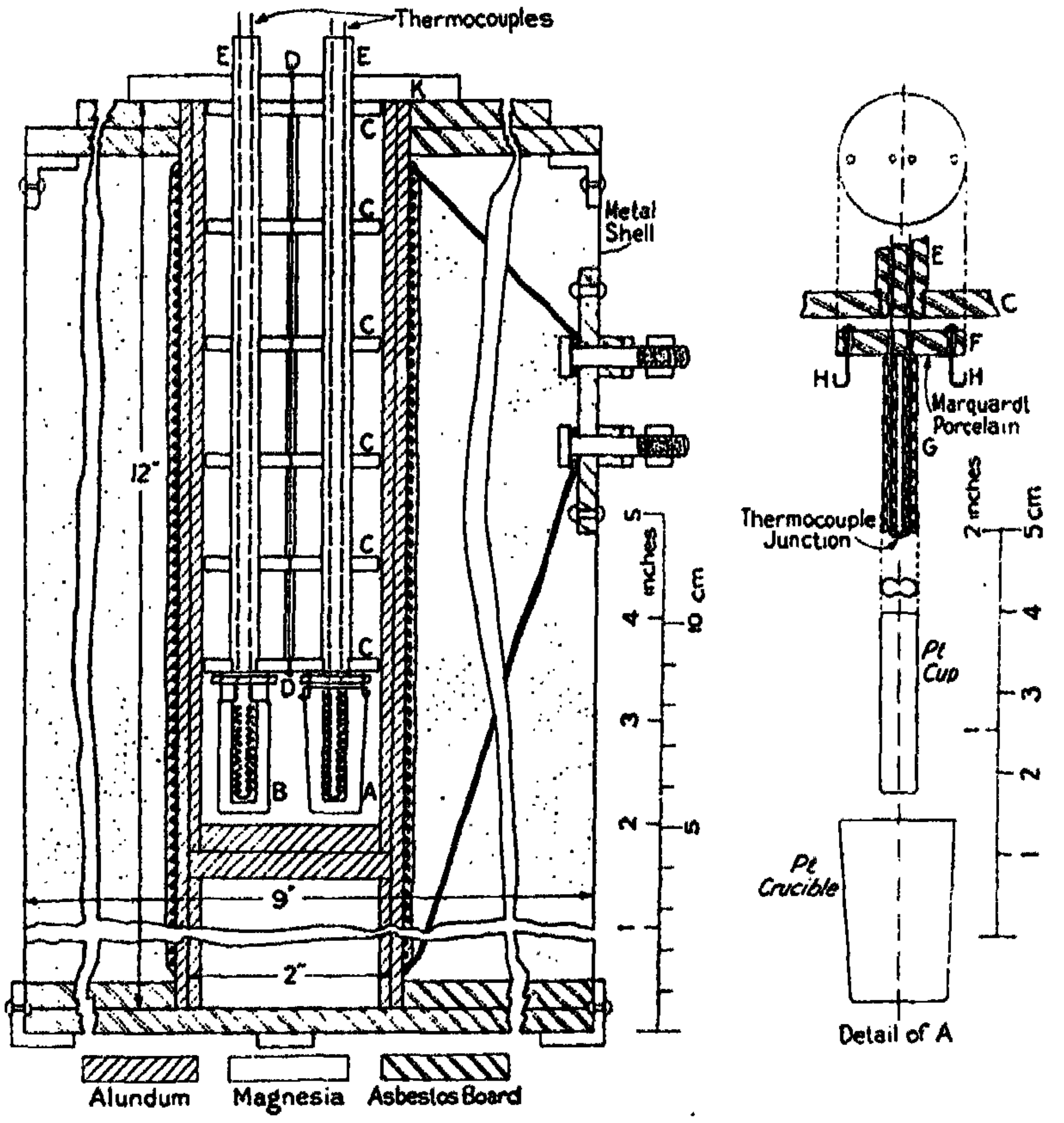

Fig. 2
The furnace and accessories.

The charge and the neutral body with their thermocouples are located in the furnace at the point where the thermal gradient is smallest. The furnace and its accessories are shown in Fig. 2, which is largely self-explanatory. The winding of the furnace consists of 20 ohms of No. 16 (B & S) nichrome type wire and consumes approximately 600 watts when connected directly on the 115 volt line. It is capable of maintaining temperatures up to 1150° with a long life. The baffles C divide the interior of the furnace into a series of chambers which are very effective in eliminating disturbances due to convection of air. The detailed assembly of *A* shows the manner in which the thermocouple is placed in the charge. The small Pt cup serves to keep the couple from being contaminated by the charge, and facilitates its removal at the close of the measurement; it is particularly useful in case the charge is melted in the crucible. In the usual arrangement when a bare couple is placed in the charge it is often impossible to remove it undamaged from the solidified melt. The present apparatus has proved entirely satisfactory not only in this work, but with heating curves of silicates as well.

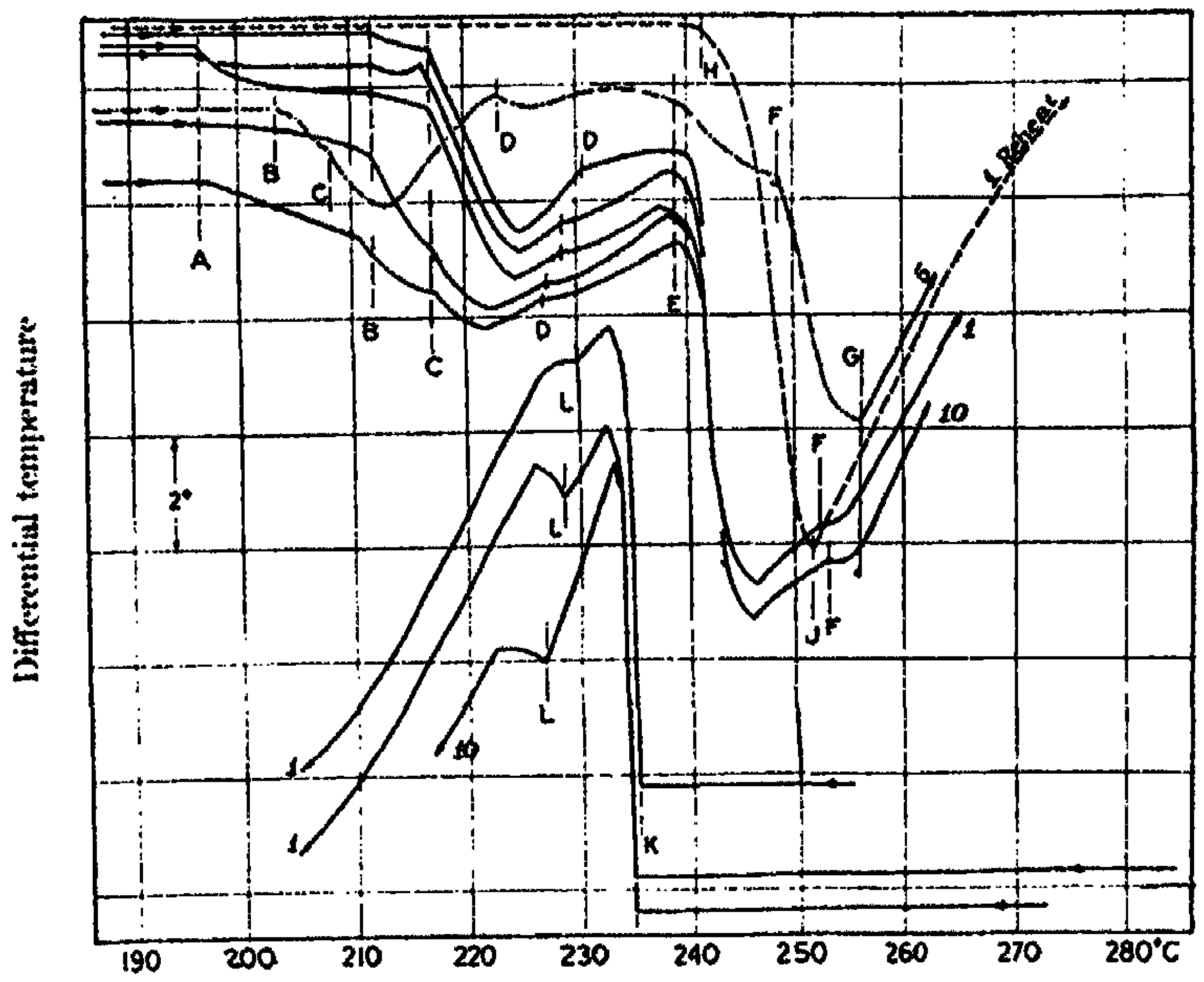

Fig. 3

Heating and cooling curves for neutral Na_2SO_4, preparations 1 and 10. Reheat curve is shown dotted, first heat curve for the slightly acid preparation 5 drawn in for comparison is indicated by the dot and dash curve. The breaks *A*, *B*, *C*, etc., denote the temperatures of the beginning of the various heat effects. Note the grouping and magnitudes of the heat effects. Compare with Figures 4 and 5.

The rate of heating or cooling is suitably controlled by periodically changing the resistance of the circuit and employing storage battery current. With some care it is possible to maintain a sensibly linear rate over periods as long as desired. The rate in ordinary runs was approximately 1° per minute; in some cases rates as low as 0.3° per minute were used successfully, particularly in the reversing experiments.

Readings of the temperature of the charge and of the differential were made alternately every half minute and appear respectively as abscissas and ordinates in the curves which follow. The results are presented in graphical form, for this is the most satisfactory way to show the position of the breaks in the curves and the relative magnitude of the heat effects obtained.

3. *Experimental Results.* In this work three distinct types of heating and cooling curves are to be distinguished for each type of preparation, namely:

(a) The first heating curve of material never previously heated beyond 100° to 125°;

(b) The cooling curve of material previously carried thru the inversions at least once;

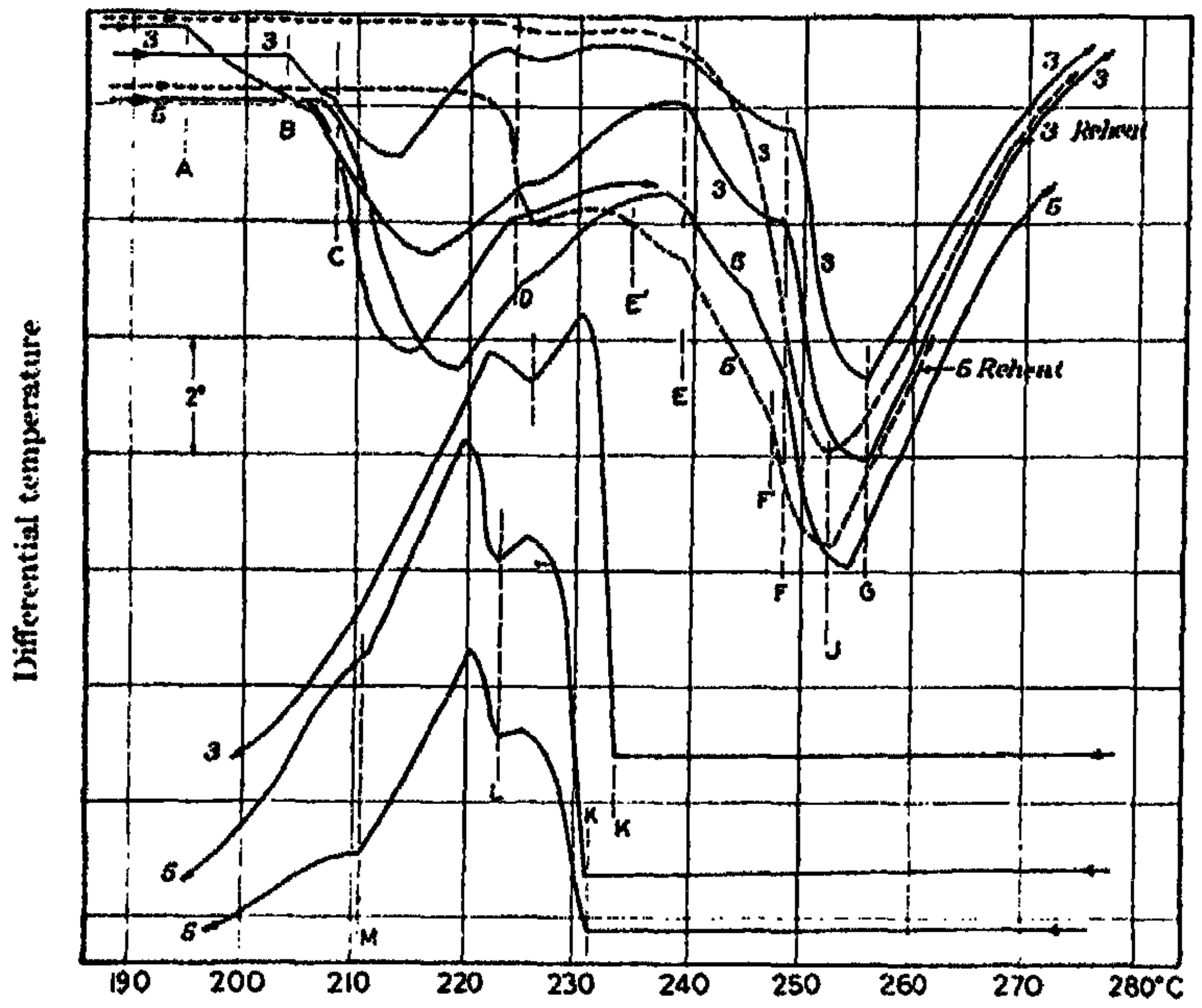

FIG. 4

Heating and cooling curves for the slightly acid Na_2SO_4 preparations 3 and 5. Reheat curves are shown dotted. Compare with Fig. 3. Note the changed contour of the reheat curves, the additional break *M* on the cooling curve of 5, and the shift in the temperatures of the beginning of the lower inversions *A*, *B*, *C*, and *D*.

(c) The reheating curve of material which has passed thru the inversion cycle at least once.

Each type of curve is characteristic, as will be seen by reference to the accompanying Figs. 3, 4 and 5. Figs. 3 and 4 present the assembly of heating, cooling and reheat curves for the neutral and the slightly acid preparations respectively, and Fig. 5 shows an assembly of first heat curves for several other types of preparations studied, together with the usual characteristic reheat curve included for reference. On these curves the breaks indicating the temperatures at which heat effects begin, whether on heating or cooling, have been marked and labeled *A*, *B*, *C* . . . etc. These have been collected and classified in Table III for the various preparations.

TABLE III

Prep.	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*J*	*K*	*L*	*M*
1	197.5	210.8	217.5	226.8	239.4	253.0	257	242	252	235	230	
	—	211.6	217.0	227.2	238.4					234.6	228.8	
	196.4	212.2	217.2	229.0	236.5	251.6				234.6	227.0	
	196.2	211.8	216	229.2	238							
	—	212	217.2	230.5	238	253.0						
2	—	212.0	217.0	231.6	237.8	255		242	251	234.7	228.2	
	—	—	216	— 235 —		—	260 ±			234.2	226.5	
	202	—	217.0	231.0	238.4	—	260 ±					
	197	—	216.5	230.3	238.6	—	260 ±					
3	195	—	206.4	224.4	238.5	248.6	258			233.8	225.8	
	—	—	206.6	224.4	238.0	247.8				233.2	225.2	
		204	208	223.5	239.5	248.5	256					
				*222					*252			
4	—	202.8	217.8	230.8	238.2	246	253.5	244	251.6	234.2	230.4	
	195.0	203.5	219.5	230.0						234.3	228.8	
5	<195	—	207	224.6	237.8	248.2	254.5					
			?	223.6								
				224.0	235.0	247.0	253.0					
	<195	201.4	206.6	222.5	—	—	—			231.0	223.0	211.6
										231.5	223.0	210.4
6		209.0	218.6	230.5	238.5	242.5	256	240	251	233.7		
7		206.0	219.0	230	237	243.6	251.5			233.8		
				230.5	237.2	242.8	251.0	240	251	233.7		
8	—	—	219.5	—	236.8	246	264					
9	—	—	—	—	—	247.5	264					
10	200.5	211.2	217	227.5	240	250	254	241	252	234.5	227.0	—
		211.5			240.5	249	253					
		211.8	217	227	238.5	251	256			234.2	226.2	
		212.0	217.5	227.5	240.5	251.5	258					
	197.4	211.8	218.3	226.7	238.4	250.5	258					
	198.0	211.9	217.4	—	—	—	—					

* Reheat.

Examination of the diagrams in connection with this table brings out the essential features of the results obtained. The first point of interest is the difference between the behavior of the salt on first heating and on reheating, the latter showing, with *neutral preparations*, merely one large heat effect beginning at a somewhat lower temperature than that of the beginning of the highest heat effect F on the first heating curve. The course of the cooling curve is no less remarkable, two adjacent heat evolutions K and L being registered with the neutral salt. The slightly *acid* preparations 3 and 5 exhibit additional features which will be discussed at a later point.

While the temperatures at which the various heat effects begin in different preparations are not definitely reproducible in all cases, there is a parallelism in the characteristics of the curves which is easily recognized. The recurrence of the heat effects is not accidental and certainly can not be ascribed to experimental uncertainties. The small irregularities in the temperatures of beginning of the various changes in heat capacity are the result of hysteresis accompanying the inversions to which the heat effects owe their origin, and are an essential feature of the results. Some of the inversions do not occur promptly, particularly on heating. The best reproducible temperature in the series, and the most prompt heat effect is that corresponding to the first break K in the cooling curve, occurring generally at 234.5° in the neutral salt. Small excess of NaOH or H_2SO_4 serves to lower this temperature to some extent. This is the temperature recorded by previous workers as representing the inversion in Na_2SO_4. The second break L on the cooling curve has heretofore escaped notice altogether.

The phase which is stable at ordinary temperature is thenardite. This is the phase which always crystallizes from aqueous solutions above 32.5° under ordinary pressure. This fact alone, however, is insufficient to afford proof of stability, because many compounds crystallize first in a metastable modification from solutions, in preference to the stable one, e.g., the calcite and aragonite forms of $CaCO_3$, etc. For this purpose thenardite and "inverted thenardite" in known amounts were sealed in glass tubes with the requisite amounts of water and oscillated in an oil bath at 50° for 18 to 24 hours. In all cases the solubilities were the same and equal to the value of 31.8 weight per cent Na_2SO_4 interpolated from the known solubility curve for this salt, at 50°. Since the solubility is not dependent upon the previous thermal history of the salt used, the phase which ordinarily crystallizes from solution, thenardite, must be the stable phase. The irreversibility noted in thermal analysis is then due to metastability, and furnishes a clear example of pseudo-monotropic behavior. This apparent irreversibility is shown convincingly by the characteristics of the first heating curves as compared with the reheat curves, the breaks A, B, C (and D) being absent upon the latter, particularly with the neutral salt.

No heat effect has been detected on heating beyond 260° and up to 700°; accordingly, Wyrouboff's qualitative estimate of 500° for the highest inversion to hexagonal form[1] is not confirmed.

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[1] See footnote, p. 1282.

The first heating curves for the *slightly alkaline* preparation 4, and the *neutral* preparations 6, 7, 8 and 9 differ from those of the slowly crystallized neutral preparations partly in the amount of energy associated with the different inversions and partly in the number of recognizable heat effects. This is particularly true of preparation 9 derived from the decahydrate.

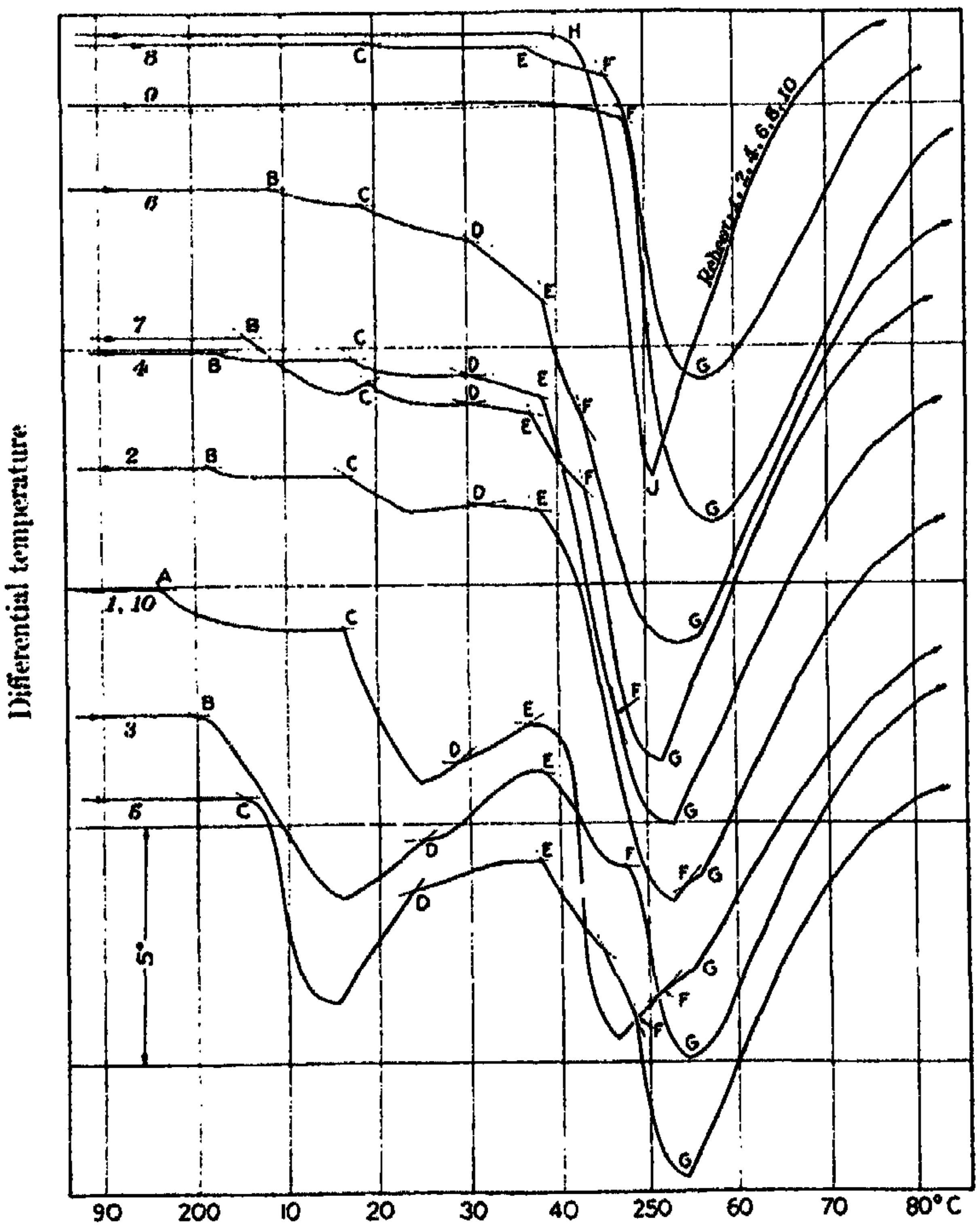

FIG. 5

The first heating curves for various preparations of Na_2SO_4, together with a typical reheat curve. Note the positions of the different breaks, and the change in the magnitude of the heat effects with relation to the amount of occluded water present. (See Table II).

Microscopic examination of these preparations shows that, as prepared, they consist principally of thenardite. (Preparations 8 and 9 were so exceedingly fine-grained that even with the highest power of the microscope the examination was difficult and the result uncertain.)

The behavior of the *slightly acid* preparations 3 and 5, as shown in Fig. 4, differs decidedly from that of the neutral preparations. All the heat effects begin at somewhat lower temperatures than in the neutral salt. The distribution of energy among the various heat effects is of different character, particularly the heat effects following the breaks *E* and *F*. The reheat curves show a reversal of the heat effect following *D* in both cases; the cooling curve of 5 also shows a well-defined heat evolution following *M*, which occurs in preparation 3 only under certain conditions (see reversal experiments). The reheat curve of 5 shows, beside the break *D*, the breaks *E* and *F*.

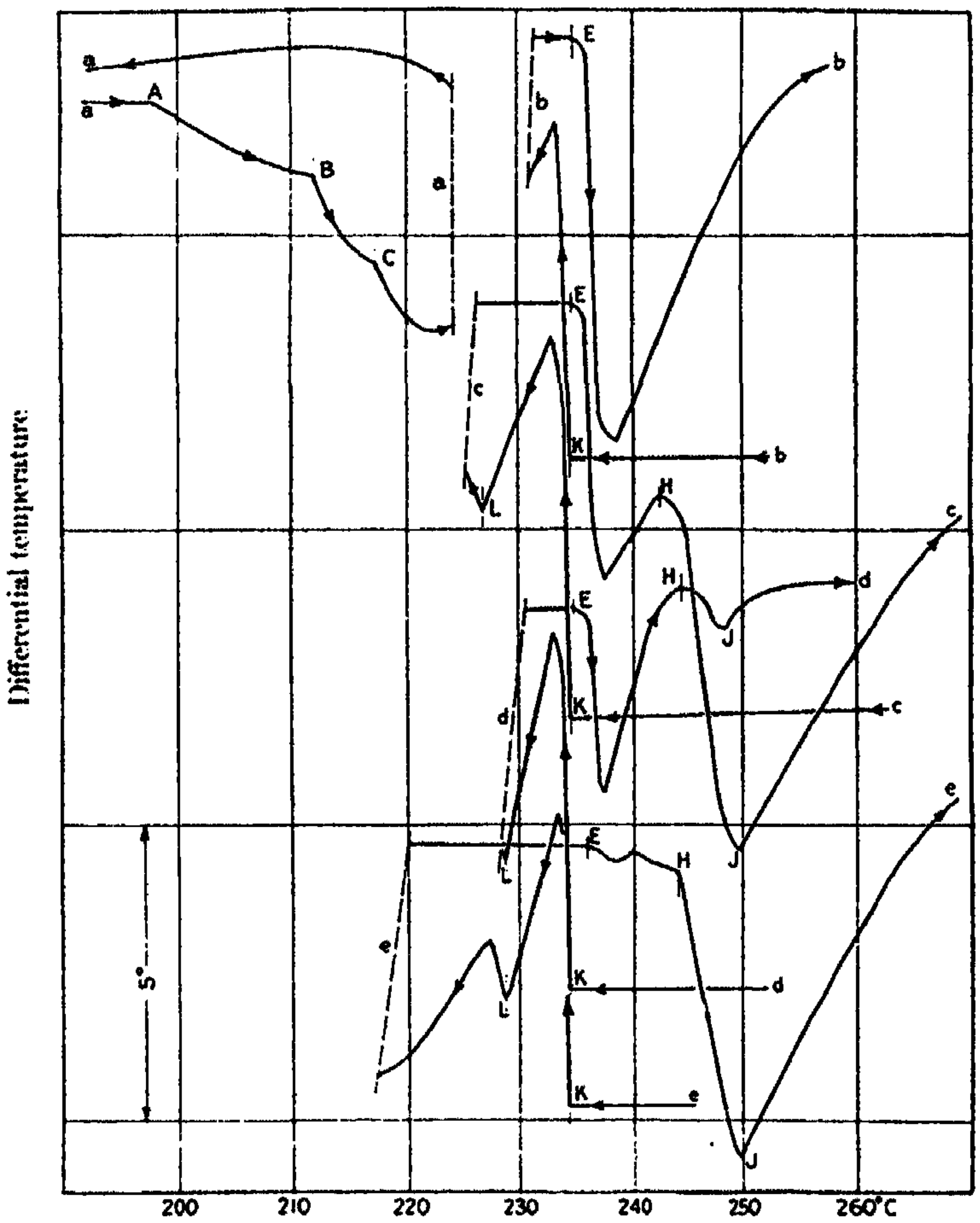

Fig. 6

The reversibility of inversions in neutral Na_2SO_4. Note that *A*, *B*, *C* (and *D*, not included in the figure) are not reversed, and the manner in which *E* and *F* occur in dependence upon how far cooling proceeds before reheating.

The first heating curves show six reproducible breaks (Fig. 3). Classified according to the amount of energy associated with the accompanying heat effects the inversions can be arbitrarily divided into two groups, the heat effects corresponding to breaks *A*, *B*, *C* (and *D*) being denoted as belonging to the lower inversions, the remaining two, *E* and *F* as belonging to the upper inversions. This arbitrary classification has some basis in fact, as will be pointed out later.

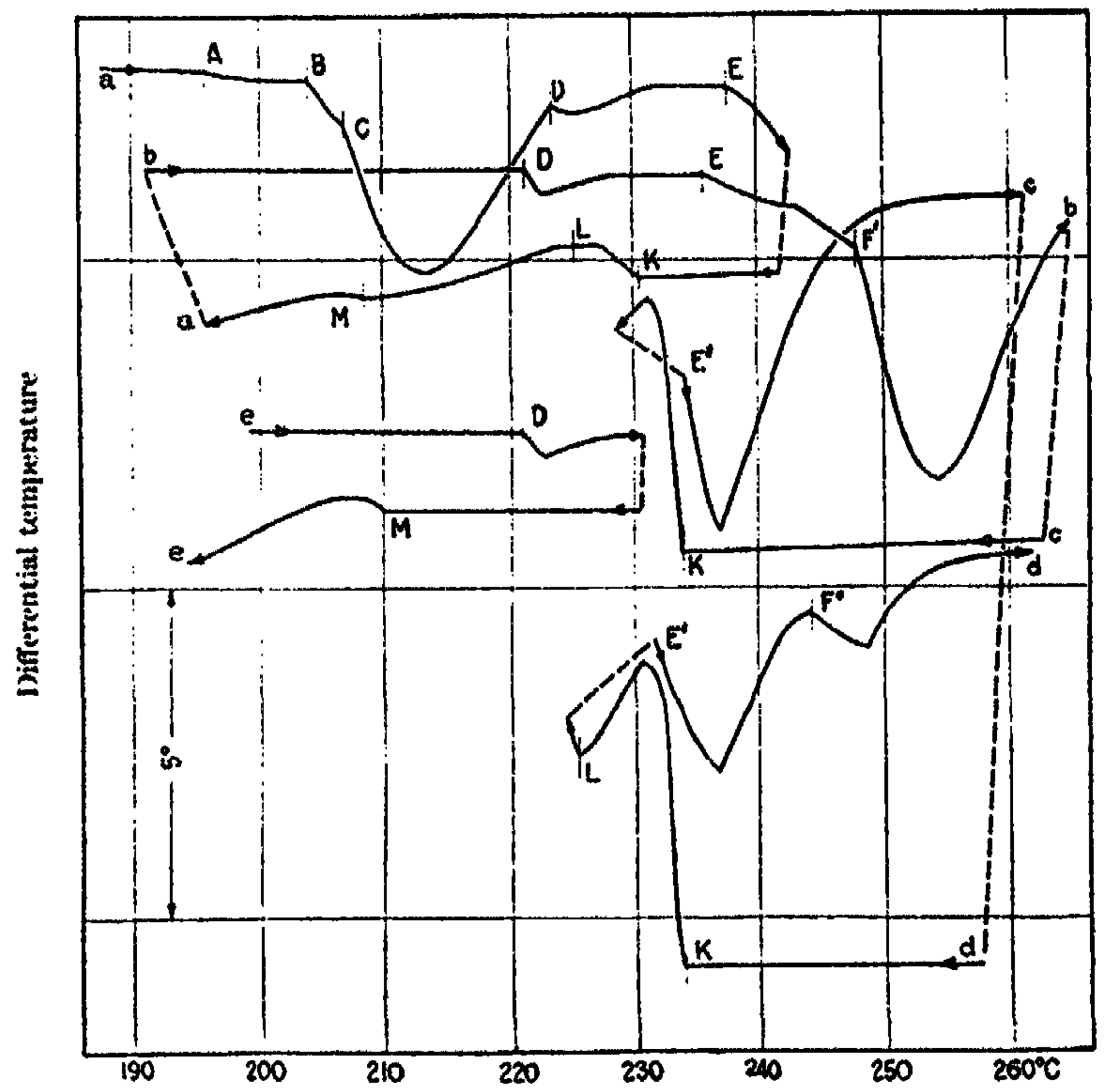

Fig. 7

Reversibility of inversions in the Na_2SO_4 preparation 3 which contained 0.1 per cent free H_2SO_4. Compare with Fig. 4. Note the irreversibility of *A*, *B* and *C*, and the small heat effect accompanying the reversal of *D* with respect to *M*. Also note the manner in which the upper inversions reverse.

4. *Reversal Experiments.* In addition to the heat runs already described, attempts were made to reverse the various inversions by quickly changing the direction of heating of the furnace. The results are shown graphically in Figs. 6, 7 and 8, and, because of their importance, are described in some detail in the following tabulation.

4.1. Preparations 1, 2, 4 and 10. Fig. 6; also consult Fig. 3.

Curve *a*. First heating. Break *A* at 198°, *B* at 212°, *C* at 217.5°. Following break *C* furnace was reversed and cooling curve recorded. No heat effects on cooling curve. Another similar first heat curve taken thru *D* at 227°; no breaks on cooling curve; not recorded in the diagram.

Curve *b*. Cooling curve from 260°. Break *K* at 234.5°.

Furnace reversed quickly before *L* takes place. Heating curve shows *E* at 236°, no other break to 260°.

Curve *c*. Cooling curve from 260°. Break *K* at 234.4°, *L* at 227°. Furnace reversed before heat effect after *L* is completed. Heating curve break *E* at 236°, break *H* (*F*) at 242.5°, major heat evolution begins at 245°. Heat effect following *H* (*F*) greater than that following *E*.

Curve *d*. Cooling curve from 260°. *K* at 234 3°, *L* at 229°. Furnace reversed immediately after *L* occurred. Heating curve shows main heat absorption after *E* at 236°, *H* (*F*) at 244.5° followed by small heat absorption.

Curve *e*. Cooling curve from 260°. *K* at 234.3°, *L* at 228.5°. Furnace reversed after heat evolution following *L* is apparently complete, and the charge has given up most of its accumulated heat. Heating curve shows meager heat effect following *E* at 236°, major effect after *H* (*F*) at 244°.

Conclusions.

1. Breaks *A*, *B*, *C* and *D* do not reverse.
2. Cooling from high temperature, *K* takes place sharply at 234.3° to 234.5°; heat evolution proceeds rapidly at almost constant temperature till heat effect is completed.
3. After cooling thru *K* a sharp reversal takes place with respect to *E* at 236°. If temperature does not fall to *L*, effect after *H* (*F*) is eliminated. If *L* occurs, *H* (*F*) occurs; the farther the heat effect after *L* proceeds toward completion the more energy is associated with *H* (*F*), the heat effect after *E* becoming less and less significant.

4.2. Preparation 3. Fig. 7; see also Fig. 4.

According to Table II this preparation contains less than 0.1 per cent H_2SO_4. The cooling curve is of the usual type, the reheat curve shows a faint effect corresponding to break *D*.

Curve *a*. First heating thru *A* at 195.5°, *B* at 203.5°, *C* at 207° and *D* at 223°. Furnace reversed immediately after break *E* occurs at 237.5°. The cooling curve then shows break *K* very much lower than usual, at 230.5° followed by a small heat effect. The level portion of this heat evolution indicates that *L* also takes place. On further cooling the recovery curve is interrupted by a heat evolution beginning at *M*, 208.5°.

Curve *b*. Furnace reversed following completion of curve *a* and heating curve taken. Break *D* occurs sharply at 221°. Heating continued thru *E* at 236°, *F′* (*F*) at 248°, until completely inverted.

Curve *c*. Cooling curve following on *b*. *K* at 234°, furnace again reversed before *L* is encountered. The following heating curve shows *E* at 234°; *F* is eliminated.

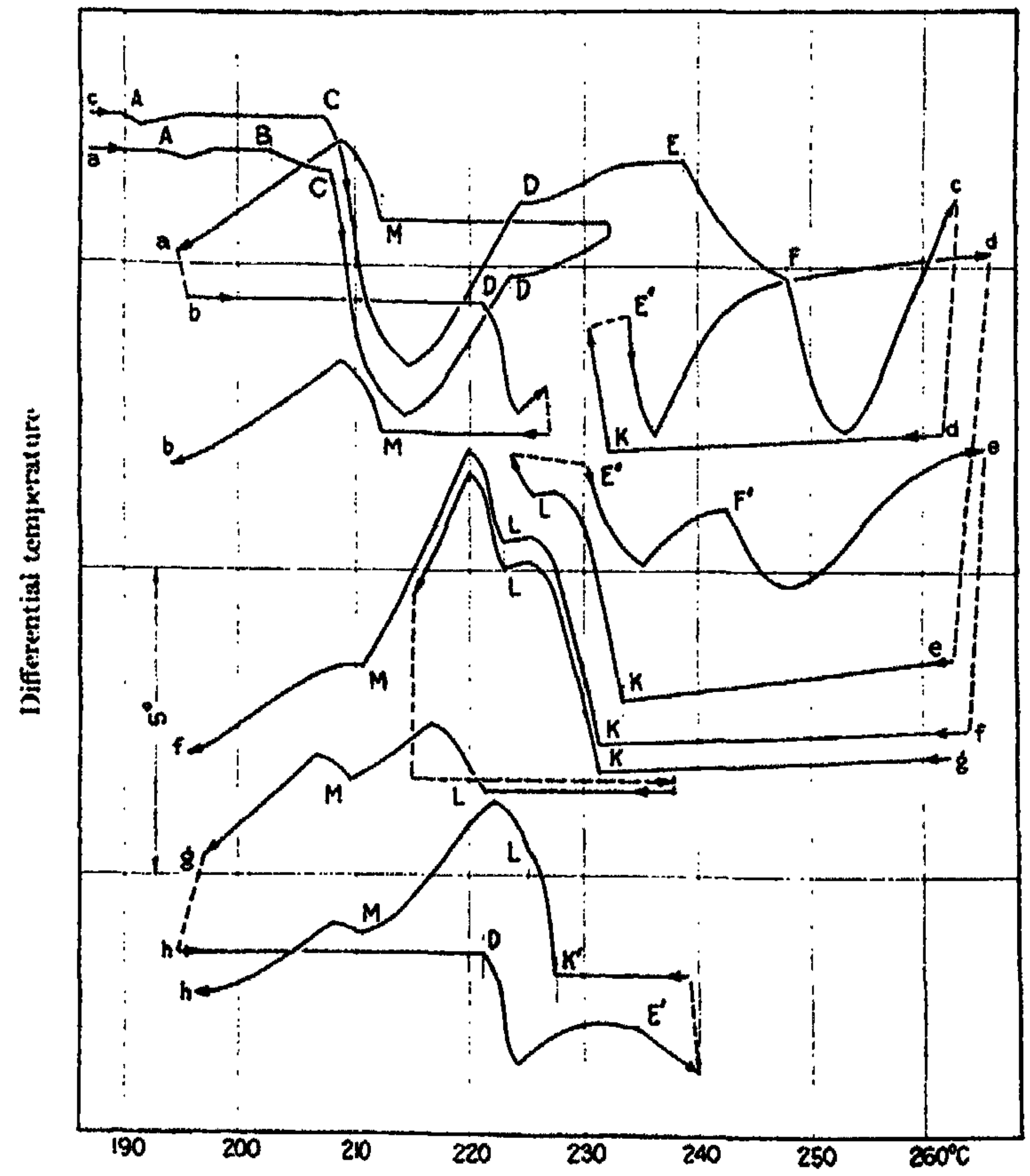

Fig. 8

The reversibility of inversions in Na_2SO_4 preparation 5 which contained 0.3 per cent free H_2SO_4. Note the irreversibility of *A*, *B* and *C*, the magnitude of the heat effect of the D ⇌ M inversion and the reversibility conditions of the upper inversions.

Curve *d*. Cooling curve thru *K* at 234°, *L* at 225.5°, furnace reversed before heat effect following on *L* is completed. Following heating curve shows a heat absorption corresponding to *E* (*E*″) whose location is indeterminate, and a heat absorption corresponding to *F* (*F*″) at 244°.

Curve *e*. Heating curve from below 180°. Only *D* on heating curve at 221°; furnace reversed, cooling curve thru *M* at 210°.

Conclusions.

1. Heat effects following on *A*, *B* and *C* do not reverse.

2. Effect *D*, while totally irreversible in the neutral salt is found at least partly reversible, the corresponding break on the cooling curve is at *M*. Hysteresis range is from 210° to 221°.
3. Heat absorption following *E* (*E'*, *E"*) on heating curve corresponds to heat evolution following *K* on the cooling curve. The reversal is prompt.
4. Break *F* (*F'*, *F"*) is lost on heating if cooling is stopped before *L* takes place.

4.3. Preparation 5. Fig. 8; see also Fig. 4.

This preparation contains about 0.3 per cent H_2SO_4.

Cooling curve shows three heat evolutions beginning at *K*, *L* and *M*. Reheat curve shows three heat absorptions beginning at *D*, *E'* and *F'*. *E'* and *F'* occur at lower temperatures than *E* and *F* on first heating curve.

Curve *a*. First heating curve thru *A* at 193°, *B* at 202.5°, *C* at 208° and *D* at 223.5°. Furnace reversed. *M* on cooling curve at 212°; no other breaks on further cooling.

Curve *b*. Heating curve following *a* thru same range of temperatures. *D* found at 221°. Furnace reversed. Cooling curve shows *M* at 212°.

Curve *c*. Complete first heating curve for comparison.

Curve *d*. Cooling curve from above 260° thru *K* at 232°. Furnace quickly reversed. Heating curve shows heat absorption following on *E"*. Owing to rapid reversal of heating the position of *E"* is indeterminate. Heat absorption proceeds with great speed at 234°. *F* is lost.

Curve *e*. Cooling curve from above 260° thru *K* at 233°, *L* at 225.5°. Furnace reversed before the heat evolution is completed. Heating curve shows heat effect following on *E"* completing at 235°, followed by another heat absorption beginning at *F"*, 243°.

Curve *f*. Cooling curve for comparison. *K* at 231.5°, *L* at 223°, *M* at 211°.

Curve *g*. Cooling curve from above 260° thru *K* at 231.5°, *L* at 223°; cooling stopped before *M* is reached. Slowly heated from 215° to 237°, followed by cooling curve. Heat evolution at 221° corresponding to *L*; *M* is at 209.5°.

Curve *h*. Following on curve *g* heating curve begins at 195°, shows *D* at 221° followed by a moderately large heat absorption, then by *E* (*E'*) at 235°. Furnace reversed quickly. Cooling curve shows *K* at 228° followed by *L* at 225°, the two heat effects partly overlapping; *M* is at 210.5°.

Conclusions.

1. Heat effects beginning at *A*, *B* and *C* do not reverse.
2. Effect beginning at *D* on heating curve is reversible and begins at *M* on cooling curve. Hysteresis range extends from 210° to 221°.

3. Heat effect beginning at *K* on cooling curve is reversible and begins at *E* on heating curve. Hysteresis range about 2°.

4. *F* is encountered on heating curves only if *L* takes place on cooling. Otherwise it is lost.

Several experiments were carried out with the aim of bringing about a reversal of the three heat effects following on *A*, *B* and *C*. Inverted samples were held at various constant temperatures between 200° and 230° for periods ranging from 12 hours up to two weeks, and heat runs were then made to determine if any appreciable inversion took place. The results were in all cases negative.

Other experiments performed with the view of reducing the hysteresis range between *D* and *M*, by holding the inverted acid preparations 3 and 5 for 12 hours at constant temperatures ranging between 212° and 220° showed that the speed of inversion is inappreciable over this region. Samples held at 211° gave the break *D* on heating, likewise samples held at 221° showed *M* on cooling.

5. *Optical Examination.*[1] Attempts were made to detect changes in the optical properties of the salt corresponding with the breaks obtained by thermal analysis. The studies with a heating microscope showed that the changes proceed slowly thru a crystal over a temperature interval, with a gradual lowering of intensity of the interference colors, with nicols crossed. No sudden changes were noticeable. This shows that the speed of the observed changes is low. Examination of samples held for some time at a particular constant temperature and then quenched gave results which further indicate that the observations of Wyrouboff and Mügge[2] are essentially correct. Thenardite heated to various constant temperatures between 195° and 215° and then rapidly cooled shows increasing quantities of a much less birefringent phase whose indices of refraction are between 1.480 and 1.485, just about equal to the high index of thenardite. This phase is identical with Wyrouboff's γ. Another phase occurs in the same samples, with greater birefringence than thenardite; its high index is about 1.480, low index is less than 1.46, and incidentally, much less than the low index of thenardite (1.47). This coincides in occurrence and appearance with Wyrouboff's β form. It always occurs mixed with thenardite (α), or the γ form; often all three phases are present. Samples of thenardite heated at constant temperatures between 220° and 230° are almost completely converted to Wyrouboff's γ with usually a trace only of the more birefringent modification remaining.

Thenardite heated for several hours above 260° should be, according to the heating curves, completely converted to the high-temperature modification. When such samples containing 2 or 3 mg. of salt are sharply quenched by dropping them into cold mercury and immediately subjected to microscopic examination, they reveal the presence of a large proportion (*ca.* 50

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[1] I am indebted to Dr. J. W. Greig for much of the microscopic work reported here. He is, however, not to be held responsible for any of the conclusions arrived at in this paper.

[2] See Table I.

per cent) of a highly birefringent modification with high index about 1.480, low index much below 1.465, together with a small amount of an apparently isotropic phase with indices lower than 1.475, the remainder being of the familiar γ. The highly birefringent phase encountered here corresponds in occurrence with Mügge's observation that Na_2SO_4 while cooling from high temperature passes thru a brief stage of higher birefringence than that of the high-temperature form or of the subsequent form which results on further cooling and which becomes inert at room temperature. Altho in general appearance and in indices of refraction this highly birefringent phase closely resembles the β modification, it is significant that the phase occurs in large amounts only in quenched samples. When the hot sample is lifted out of the furnace and cooled in air this phase disappears almost completely. These observations agree with the presence of the breaks K and L on the cooling curves, and also in that the heat effects following K and L, particularly the former, are very prompt. On these considerations it appears that the nearly isotropic phase of index less than 1.475 must be the high temperature (hexagonal) form denoted as δ by Wyrouboff, and that the highly birefringent form occurring in the quenched samples is the same as that observed by Mügge, with its stability range between those of Wyrouboff's γ and δ.

These studies, when considered with the results of thermal analysis make the assumption of pentamorphism in Na_2SO_4 tenable; in fact, it is not possible to correlate all the experimental data on the basis of a smaller number of phases.

Discussion

1. *Theoretical.* For the purpose of clarity it seems desirable to recall here the more important principles involved in the theoretical treatment of the equilibrium conditions governing inversions.

In a polycomponent system of two or more phases coexisting *in equilibrium* the chemical potential μ of each actual component has the same value in all the phases. In a system of one component μ is equal to the molar thermodynamic potential of that component. The slope of μ for a given phase as a function of temperature is given by the molar entropy of that phase,

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,m} = -S;$$

that is, for the coexistence of two phases in equilibrium at the equilibrium temperature

$$\mu_{I} = \mu_{II}$$

$$\left(\frac{\partial \mu_{I}}{\partial T}\right)_{p,m} - \left(\frac{\partial \mu_{II}}{\partial T}\right)_{p,m} = S_{II} - S_{I}$$

At the equilibrium temperature

$$S_{II} - S_{I} = \frac{\Delta H}{T_i}$$

where ΔH is the change in the heat content of phase II on conversion into phase I, numerically equal to the heat of inversion at constant pressure, and T_i is the equilibrium inversion temperature.

The stable phase is always characterized by the lower value of μ. If phase I is stable at the higher temperature, then, in the event of inversion, below the equilibrium temperature $\mu_{II} < \mu_I$, while above the equilibrium $\mu_{II} > \mu_I$. Below the inversion temperature the reaction II → I can not take place. At the equilibrium temperature, where $\mu_{II} = \mu_I$ the reaction proceeds infinitely slowly. It reaches a measurable speed only when the value of the potential difference $\mu_{II} - \mu_I$ has attained sufficient magnitude to overcome the forces of restraint within the crystal operative virtually as internal friction. This imparts to the system a kind of inertia or hysteresis, which appears as apparent superheating or undercooling. Whether it is justifiable to speak of superheating and undercooling in the case of inversions remains to be decided by experiment. It is certain that the low to high inversion in quartz recently re-investigated by Gibson[1] is the only known case of apparently well substantiated superheating on inversion.

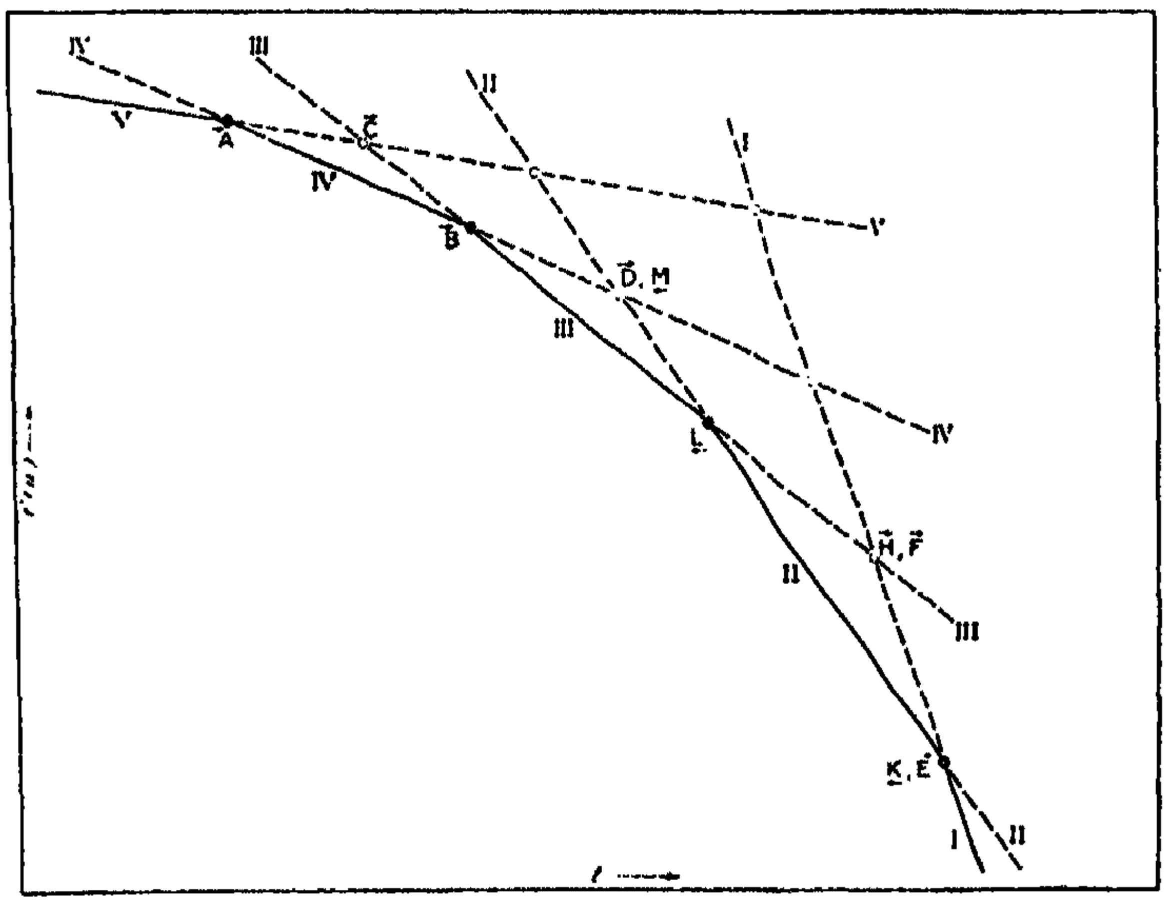

Fig. 9
Equilibrium diagram for pentamorphism applied to the case of Na_2SO_4. See Table IV and the text.

When a substance is capable of existence in more than two modifications the complexity of behavior increases rapidly with the number of possible phases. The total number of possible stable and metastable inversions is

$$1 + 2 + \ldots\ldots\ldots\ldots + (n - 1)$$

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[1] R. E. Gibson: J. Phys. Chem., 32, 1197, 1206 (1928).

where n is the number of possible crystalline phases.[1] The stable inversions number $n-1$. All the rest are metastable.

2. *The system* Na_2SO_4. In describing the experimental results it was pointed out that the facts are best accounted for on the basis of pentamorphism of Na_2SO_4. I shall now attempt to give a justification for this assertion.

In Fig. 9 is given a schematic diagram of thermodynamic potential μ as a function of temperature for five mutually convertible phases, arbitrarily employing a straight line relationship between μ and t. The lines intersect at the theoretical inversion temperatures with no hysteresis. The position of the μ lines for the various phases is fixed in agreement with the equations on p. 1299. In accord with the current convention of petrography, the phases are numbered with Roman numerals beginning with the phase stable at high temperature. The various intersections are labeled A, B, C, etc. to accord with the breaks encountered on the heating and cooling curves in the experiments on reversibility and the optical studies.

The established facts may be interpreted as follows:

1. Reactions beginning at A, B and C on first heating curves do not reverse. Thenardite is stable at low temperatures, hence these phase reactions are pseudo-monotropic. Under a heating microscope, the reactions are seen to be sluggish. Instead of taking place rapidly throughout a crystal at appreciably constant temperature, the formation of a new phase spreads slowly thru the crystal, occupying a considerable temperature interval. Because of the very considerable hysteresis the reactions can proceed simultaneously, the breaks on the heating curves merely marking the temperatures at which each reaction has attained sufficient speed to begin to absorb appreciable quantities of heat.

2. The reaction beginning at D does not reverse in neutral or slightly alkaline salt; in slightly acid salt it reverses at M, with a hysteresis range of about 12°.

3. Reaction beginning at K on cooling curves reverses at E on heating curves. This reaction shows comparatively little hysteresis, and takes place promptly, particularly on cooling. It is interpreted as representing the inversion of the high temperature modification into the next stable form, that is, $I \leftrightarrows II$.

4. The appearance of F on heating curves depends on whether the preceding cooling curve in reversibility experiments had proceeded as far as L. When the reaction following L goes to completion, E is eliminated, as is seen from the reheat curves of neutral preparations. The form following L on the cooling curve is Wyrouboff's γ; but the simplest tenable assumption is that L must represent the inversion of $II \rightarrow III$. Reheat curves for the neutral salt show that H (F) represents the inversion of Wyrouboff's γ to the high-temperature form; accordingly we have

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[1] True monotropic inversions are not considered.

L = II → III, F = III → I, identifying Wyrouboff's γ with the form numbered III in the present scheme.

5. The arbitrary classification of the heat effects into two groups, comprising the lower inversions (A, B, C) and the upper inversions (E, F, K. L). alluded to earlier in the paper (p. 1294) is now justified on the basis that the lower inversions are pseudo-monotropic while the upper inversions are more readily reversible. The inversion $D \leftrightarrows M$ is reversible only in the slightly acidified preparations; it fits into the scheme on the assumption that it represents the metastable transition IV ⇆ II. In neutral preparations the breaks M on the cooling curve, and D and E on the reheat curve are eliminated, and no modification lower than III is formed on cooling. If II is the highly birefringent Mügge form with but a brief temperature interval of existence, then IV is the Wyrouboff β. Thenardite, the ordinary low-temperature modification, becomes form V in this scheme.

Table IV

1. *Identification of Phases*

Phase I	High temperature modification, observed by Mügge, named δ by Wyrouboff.
Phase II	Highly birefringent phase of brief stable temperature interval resulting from the high temperature modification, observed by Mügge.
Phase III	"Altered thenardite" observed by Mügge, named γ by Wyrouboff. Inert at ordinary temperature.
Phase IV	Wyrouboff's β.
Phase V	Thenardite, Wyrouboff's α.

2. *Identification of Inversions*

Break	Phase Change	Temperature °C.	
		Heating Curve	Cooling Curve
A	V→IV pseudo-monotropic	197 ± 2 (neutral) 195 ± 2 (acid)	——
B	IV→III pseudo-monotropic	210 ± 2 (neutral) 202 ± 2 (acid)	——
C	V→III pseudo-monotropic	217 ± 2 (neutral) 207 ± 2 (acid)	——
D, M	IV⇆II	230 ± 2 (neutral) 222 ± 1 (acid)	Irreversible in neutral 210 ± 2 (acid)
E, K	II⇆I	238 ± 2 (neutral) 236 ± 2 (acid)	234.5 ± 0.1 (neutral) 233 ± 1 (acid)
F (H)	III→I	244 – 250	——
L	II→III	——	228 (neutral) 225 (acid)

The presence of traces of H_2O in the inclusions, and particularly the presence of small amounts of H_2SO_4, greatly increases the facility with which the inversions take place. It has already been remarked that the amount of energy associated with the various heat effects differs according to the mode of preparation of the salt. The behavior of the slightly acidified preparations 3 and 5 is unique in this respect. The breaks take place at lower temperatures than in neutral salt. Reluctance toward inversion is decreased to such an extent that $D \leftrightarrows M$ can take place. It is plausible that the role played by the occluded water is that of enabling the lower inversions to proceed; it is certain that when this water is eliminated by previous heating the lower inversions do not reverse, and also in preparations with very low H_2O content the lower heat effects on first heating are less energetic (see Fig. 5, preparations 4, 6, 7, 8, 9).

Conclusion and Summary

The close proximity of the inversions, the large hysteresis and the tendency toward pseudo-monotropic behavior of some of the inversions serve to make this unary system of outstanding importance in the elucidation of the theory of solid state. The conclusions deduced from this preliminary investigation are that Na_2SO_4 is capable of existence in five distinct modifications, the scheme of inversions being made evident in Fig. 9. Owing to hysteresis in the inversions the equilibrium temperatures can not be fixed; the same holds true for the stability intervals of the various phases. The essential conclusions are summarized in Table IV, the temperatures given representing values at which each inversion proceeds with sufficient speed to produce an appreciable heat effect.

Acknowledgment

I wish to express my thanks to my colleagues R. E. Gibson, J. W. Greig, E. Posnjak, G. Tunell, and C. J. Ksanda for aid in connection with various phases of this work.

Geophysical Laboratory,
Carnegie Institution of Washington,
May, 1929.

THE POLYMORPHISM OF SODIUM SULFATE: II. THE DENSITIES OF ANHYDROUS SODIUM SULFATE AT 25°

BY F. C. KRACEK AND R. E. GIBSON

Introduction

From observations of heating and cooling curves for anhydrous sodium sulfate crystallized by several methods Kracek[1] showed that this salt exhibits complex polymorphism over the temperature interval from 190° to 250°C. Correlation of these observations with the results of microscopic examination, by Mügge[2] and Wyrouboff,[3] supplemented by his own microscopic studies, led him to the conclusion that Na_2SO_4 can exist in five modifications, some of which exhibit pseudo-monotropic behavior while others can be readily inverted in the dry state. The form of anhydrous sodium sulfate stable at ordinary temperature is known as thenardite. When this is passed thru a complete cycle of inversions, the resulting product exhibits optical properties which differ significantly from those of thenardite. This modification has been termed "*inverted thenardite*" by Mügge, γ by Wyrouboff, and corresponds to form III on the scheme of polymorphism advanced by Kracek, thenardite being form V. As the conversion of thenardite to form III is undoubtedly accompanied by a volume change, it is reasonable to suppose that the density of a sample of Na_2SO_4 should depend upon its previous thermal history, and in particular, on whether or not the sample had been heated above 200°C.

Earlier determinations of the density of Na_2SO_4 are summarized in Mellor.[4] The results vary from 2.629 according to Filhol to 2.7 according to Schröder. The more important values lie between 2.65 and 2.7. The uncertainty in these results is considerably more than the probable error of determination, and seems to indicate an uncertainty of the nature of the samples investigated. The most accurate determination of the density of anhydrous sodium sulfate is that of Richards and Hoover,[5] who found that sodium sulfate which had been heated to the point of fusion gave, on the average, 2.698 ± .002 for the density at 30°. Wyrouboff (op. cit.) found 2.696 for ignited Na_2SO_4.

In this work we have determined the densities of several preparations of pure anhydrous sodium sulfate whose careers have been carefully watched from the time the salt was crystallized.

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[1] J. Phys. Chem., **33**, 1281 (1929).

[2] Mügge: Neues Jahrb. Mineral. Geol., **1884**, (2), 1-14.

[3] Wyrouboff: Bull. Soc. min. France, **13**, 311-6 (1890).

[4] Mellor: "Comprehensive Treatise on Theoretical and Inorganic Chemistry," **2**, 662.

[5] Richards and Hoover: J. Am. Chem. Soc., **37**, 108 (1915).

Experimental

The material used in these experiments was derived from J. T. Baker's C.P. Analyzed Anhydrous Sodium Sulfate and from Kahlbaum's Anhydrous Sodium Sulfate. It was essential to secure well-crystallized material which was as free as possible from liquid inclusions. Methods for preparing crystals of anhydrous sodium sulfate have already been discussed in the preceding paper of this series and indeed the preparations used in this work were among those used in the thermal analysis. For the sake of clearness, however, we shall repeat briefly descriptions of the preparations whose densities are given in Table I.

Preparation 1 consisted of small and irregular crystals of Na_2SO_4 grown from a solution at 70°. The solution was not covered and the crystals separated as a crust on the surface. On ignition the material lost 0.1 per cent water. Preparations 2 and 3 consisted of large crystals grown slowly at 70°-80° in a covered vessel. On ignition they lost 0.03 per cent water. Preparation 4 was made in the same way as Preparation 2 except that the solution was alkaline to an extent of $2 \times 10^{-3}N$. The crystals lost no water on ignition and did not give an alkaline reaction. Preparation 5 was similarly obtained from a solution containing $1 \times 10^{-2}N$ H_2SO_4. It lost 0.024 per cent of water on ignition, and contained 0.3 per cent H_2SO_4.

In all cases the solid was separated from the supernatant liquor by suction filtration or by decantation, dried at about 100° for many days and divided, after careful crushing, into various sizes by appropriate sieves. A sample, usually of the 10–28 mesh size, was then taken and divided into two parts. On one portion density measurements were made immediately. The other portion was heated to 300°-400° in a platinum vessel and the loss of water during ignition was noted. The sample was cooled and its density determined. The ignited portions of each preparation are indicated with an *A* if cooled slowly after heating and an *A'* if cooled rapidly. Thus, samples 2, 2*A* and 2*A'* were taken from the same preparation, sample 2 was never heated beyond 100°, sample 2*A* was heated to 300°-400° and cooled slowly and sample 2*A'* was heated to the same temperature and cooled rapidly. Part of preparation 2 was fused carefully at 885° and cooled very slowly to room temperature. A fine clear crystalline product, fused Na_2SO_4, was obtained.

For the density determinations flat-topped pycnometers of the type described by Johnston and Adams[1] were used. The balance, weights, thermostat, multiple junction thermocouple and potentiometer used in connection with the thermostat have been referred to in previous papers.[2] Experiments were made at 25° ± 0.01°C. Xylene was used as the displaced liquid and its density, determined by comparison with pure water, was found to be 0.8520, 0.8520 and 0.8519 grams per millilitre. The specific volume was, therefore, 1.1737 ml. per gram. The experimental results were corrected for buoyancy of the air by the formula proposed by Johnston and Adams.

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[1] Johnston and Adams: J. Am. Chem. Soc., 34, 563 (1912).

[2] Gibson: J. Phys. Chem., 31, 496 (1927).

TABLE I

Density of Na_2SO_4 at 25.00 ± 0.1°C

Preparation	% H_2O occluded	Wt. of Na_2SO_4	Vol. of xylene displaced	Uncorrected density	Density corrected for buoyancy	Density corrected for occluded H_2O
1	0.103	13.1105	4.9300	2.6593	2.6568	2.661
2	0.028	16.4405	6.1712	2.6640	2.6615	2.663
3	0.040	14.7629	5.5437	2.6630	2.6605	2.663
4	0.000	13.8350	5.1860	2.6678	2.6653	2.665
5	0.024	13.6384	5.1239	2.6617	2.6592	2.661

Density of Na_2SO_4 dried at about 100°, av. = 2.662_5

Av. for 2, 3 and 4 = 2.664 ± 0.001

1*A*		11.3343	4.2096	2.6925	2.6899	2.690
2*A*		16.1144	5.9799	2.6948	2.6922	2.692
2*A'*		17.6678	6.5553	2.6951	2.6925	2.692
3*A*		15.9156	5.9118	2.6921	2.6895	2.690
4*A*		14.0163	5.1935	2.6988	2.6962	2.696_2
5*A*		17.3482	6.4502	2.6896	2.6870	2.687
5*A'*		15.1407	5.6267	2.6909	2.6883	2.688
Fused		18.7643	6.9504	2.6997	2.6971	2.697_1

Density of ignited Na_2SO_4, gross av. = 2.692

Av. for 4*A* and Fused = 2.697 ± 0.001

Discussion of Results

The accuracy of the foregoing results is strictly limited by our inability to prepare from solutions crystals of anhydrous sodium sulfate which were entirely free from inclusions. In the case of the unignited material an approximate correction for the volume of the water included was applied, bringing the results for preparations 2, 3 and 4 to an average value of 2.664 ± 0.001. The results for preparations 1 and 5 are lower; the amount of included water in preparation 1 makes the correction uncertain, while 5 contains about 0.3 per cent H_2SO_4 (determined by titration of a sample with standard alkali), and hence, is not strictly pure Na_2SO_4. Ignited preparation 5 also yields lower density than the others. Our best result is that for preparation 4 which contained so little occluded water that the loss of weight on ignition could not be measured, but even this material contained some microscopic inclusions. In the case of the ignited preparations the results are vitiated by the uncertainty of filling of the cavities resulting from the inclusions, with xylene. It is significant that the values for preparation 4 and for the fused Na_2SO_4 agree closely while all the others give lower densities.

In view of these considerations we estimate the density of the unignited crystals (thenardite, Na_2SO_4 V) as 2.664 ± 0.001, and that of the ignited, cooled crystals (Na_2SO_4 III) as 2.697 ± 0.001, at 25.00 ± 0.01°C. The latter value checks closely with the best published determinations.

The purity and homogeneity of the preparations used were checked by careful microscopic examination for which we are indebted to Dr. J. W. Greig. Very little information could be obtained on the nature of the inclusions. These are generally so minute in size that even with the highest power of the microscope it was not possible to tell whether they were filled with liquid or air after ignition. The nature of the phases present could be told with certainty for the modifications V and III. The samples examined before ignition consisted of thenardite (Na_2SO_4 V) with only traces of other material. After ignition, and in the case of the fused sample, the bulk of the material was Na_2SO_4 III. Another phase was usually present, in amount from a trace to perhaps as much as 1 per cent in preparation 5. This phase resembles thenardite but has higher birefringence; its low index is considerably lower than the low index of thenardite. The differentiation between the two is difficult when they are present in small quantities mixed with a large amount of modification III. This highly birefringent phase has been classified as modification IV in the first paper of this series.

Conclusion

The results of this investigation show clearly that Na_2SO_4 can exist at ordinary temperatures in at least two modifications. One of these is the ordinary low-temperature form, thenardite (Na_2SO_4 V), with a density of 2.664 ± 0.001. When this is heated above 200° it becomes altered, passing through a series of polymorphic changes, as indicated in the first paper. On subsequent cooling the salt does not revert to thenardite, if kept dry, but remains in the form of another modification, Na_2SO_4 III, which has the density 2.697 ± 0.001. In this connection result $2A'$ is of interest as the density determination was made one week after the preparation was ignited. In the preceding paper of this series it was also shown that Na_2SO_4 kept after a cycle of inversions at various temperatures below 200° failed to invert to the low temperature form.

The volume change accompanying the mutual conversion of these two phases is 0.0045 cm^3/g or 1.2 per cent of the volume of Na_2SO_4 V at 25°. If the two modifications have sensibly equal coefficients of expansion up to the inversion point we should expect a contraction of approximately 1.2 per cent when the reaction takes place.

These density results have been combined with microscopic examination, and furnish a confirmation of the results of thermal study of this salt presented in the preceding paper. They are in accord with reliable data, both optical and on densities, published by other investigators. In view of the known stability of thenardite (Na_2SO_4 V) they firmly establish the pseudo-monotropic nature of the mutual conversion in the dry state of the two modifications discussed.

Much vague discussion has appeared in print on the metastability of matter. The phenomena involved are neither vague nor mysterious, and, admittedly, they abound in nature to a greater extent than has for long been suspected. Accurate work is required in their investigation, but more than that, a varied attack is necessary, for phenomena which escape interpretation in one mode of attack can often be elucidated by a combination of methods. To take as example the present work on densities; alone it would have little meaning. Combined with optical examination, thermal analysis, and the other methods employed, the results fall in line with a consistent scheme. The next paper of this series will deal with dilatometric measurements.

Summary

At least two modifications of anhydrous sodium sulfate can exist indefinitely at ordinary temperature and pressure. These forms, thenardite or Na_2SO_4 V, and Na_2SO_4 III have at 25.00 ± 0.01°C densities of 2.664 ± 0.001 and 2.697 ± 0.001 respectively.

Geophysical Laboratory,
Carnegie Institution of Washington,
May, 1929.

PARTIAL PRESSURES OF BINARY SOLUTIONS*

BY RALPH W. DORNTE

Introductory

The problem of solutions is one which has been studied for many years although at the present time an adequate theory is still lacking. The partial pressures of the volatile components of a binary solution of liquids have frequently been used to study the nature of solutions. In 1887, Raoult[1] found empirically a relation involving the partial pressure of a volatile solvent and the concentration of a non-volatile solute. Raoult's original relation is expressed by the equation,

$$\frac{N_1}{N_2} = k\frac{P_2 - P_2'}{P_2}$$

where N_1 is the number of mols of the solute dissolved in N_2 mols of solvent, P_2 the vapor pressure of the pure solvent and P_2' its partial pressure in the solution. The mol ratio in the first term refers to the molecular weights in solution. The equation referred to as Raoult's law is

$$\frac{N_1}{N_1 + N_2} = \frac{P_2 - P_2'}{P_2} \qquad (1)$$

For ideal solutions this relation gives accurately the partial pressures over the entire range of concentrations. In an ideal solution there is no heat effect and no volume change accompanying the mixing of the components. In this case each component has the same molecular weight in the pure liquid as in the solution and vapor. Raoult's law is obviously the expression for the change in the partial pressure of one component as its concentration in the liquid phase is changed by another component whose only effect is dilution. When the partial pressure of the volatile component is plotted against the composition of the liquid phase, Raoult's law gives a straight line joining the zero and the vapor pressure of the pure component. For ideal solutions of two volatile liquids, Raoult's law gives accurately the partial pressure of either component over the entire range of concentrations. The number of ideal solutions of two volatile components is relatively small. For most solutions it is applicable in the range of the so-called dilute solutions, but fails even as a good approximation for 80% of the entire concentration range.

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[1] Compt. rend., **104**, 1430 (1887).

The Duhem-Margules equation was first deduced thermodynamically by Duhem[1] and may be expressed,

$$\frac{d \ln P_1}{d \ln x} = \frac{d \ln P_2}{d \ln(1-x)} \tag{2}$$

where P_1 and P_2 are the partial pressures of the two components, x and $1-x$ are their respective concentrations in the liquid phase expressed in mol fraction. The molecular weights involved in the mol fraction are referred to those in the vapor. Margules has shown that this equation is only integrable when the relations between P_1 and x and between P_2 and $1-x$ are known and found that the equation is satisfied by,

$$P_1 = P_1^\circ x^a$$

and

$$P_2 = P_2^\circ (1-x)^a$$

and P_1° and P_2° are the vapor pressures of pure components and a an empirical constant. Lehfeldt[2] undertook the experimental verification of this equation and obtained quite satisfactory agreement in certain cases. Margules then showed that this equation did not correspond entirely to the physical conditions and proposed a more complex form which, by introducing Raoult's law, Zawidski[3] reduced to the form:

$$P_1 = P_1^\circ x\, e^{\frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3}$$

$$P_2 = P_2^\circ (1-x) e^{\frac{\beta_2}{2} x^2 + \frac{\beta_3}{3} x^3}$$

These equations agreed well with the data for certain solutions but none too well for associated liquids.

Professor Bancroft[4] has found empirically that the equation,

$$a \log \frac{G_1}{G_2} = \log \frac{P_2 - P_2'}{P_2} + \log K_1$$

represents the data remarkably well over the entire range of concentrations. From Raoult's law,

$$\frac{N_1}{N_1 + N_2} = \frac{P_2 - P_2'}{P_2}$$

the following equation is obtained algebraically:

$$\frac{G_1 M_2}{G_2 M_1} = \frac{N_1}{N_2} = \frac{P_2 - P_2'}{P_2'} \tag{3}$$

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[1] Ann. de l'Ecole normale sup., (3) 4, 9 (1887).

[2] Phil. Mag., (5) 46, 42 (1898).

[3] Z. physik. Chem., 35, 129 (1900).

[4] Proc. Nat. Acad. Sci., 15, 8 (1929).

where M_1 and M_2 are the gram molecular weights of the components in the vapor, and G_1 and G_2 are the grams of the components in the liquid phase. *By introducing two empirical constants, a and K, the equation is obtained.*

$$\left(\frac{G_1M_2}{G_2M_1}\right)^a = \left(\frac{N_1}{N_2}\right)^a = K\,\frac{P_2 - P_2'}{P_2'} \tag{4}$$

or

$$a \log \frac{G_1}{G_2} - \log \frac{P_2 - P_2'}{P_2} = \log K \tag{5}$$

Bancroft and Davis[1] have found that this equation represents very well the data by Dobson[2] for the system ethyl alcohol-water at 25°C. The calculated partial pressures of water agree with the experimental values within the limits of experimental error for all concentrations up to 78%. The values for alcohol agree very well except for the most concentrated solution and the two most dilute solutions. The data by Ferguson and Funnell[3] on methyl and water are represented fairly well by the equation. Morton's[4] data for the systems methyl alcohol-water and acetone-methyl alcohol are given by the equation within the limits of experimental error except the partial pressures of water in the acetone-water system. The values calculated from the equation for the system acetone-ether agree excellently with the data by Sameshima[5] except for the partial pressures of ether. The deviations in this case are well beyond the experimental error. These are the only systems to which equation (5) has been applied at present. Reliable data on partial pressures are available for only a few systems.

Experimental

The purpose of this investigation is two-fold: (1) To test the validity of equation (5) for other binary systems, (2) to study the applicability of the gas interferometer to the determination of vapor compositions in equilibrium with binary solutions of volatile liquids. The system ethly alcohol-water at 25°C was chosen since Dobson's data are available for comparison. As a check on the interferometer method a distillation procedure was also used in this work.

The previous methods for partial pressures of binary systems may be divided into two groups: (1) Dynamic methods; and (2) Static methods. Most investigators have employed a dynamic method, either distilling at constant temperature or saturating a known volume of air by bubbling it through the solution. Static methods depend upon the determination of some physical property of the vapor phase to obtain its composition. Very little effort has been made by the various investigators to reconcile the

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[1] J. Phys. Chem., **33**, 361 (1929).

[2] J. Chem. Soc., **27**, 2866 (1925).

[3] J. Phys. Chem., **33**, 1 (1929).

[4] J. Phys. Chem., **33**, 384 (1929).

[5] J. Am. Chem. Soc., **40**, 1482 (1918).

results of one method with those of another. The static method is more readily applied to pure substances or systems with one volatile component than to systems with two volatile components.

Zawidski[1] and Wrewsky[2] used a distillation method at constant temperature; Rosanoff and Easly[3] distilled at constant pressure. Sameshima used a refluxing distillation procedure at constant temperature and obtained satisfactory results. Schmidt[4] points out several disadvantages in the distillation procedure, namely; overheating and the dependence of vapor pressure and composition upon the rate of heating. Ferguson and Funnell have very recently used an elaborate apparatus to circulate the vapor over the liquid.

Regnault[5] first employed the air-bubbling method for the vapor pressure of water. Will and Bredig[6] and Orndorff and Carrell[7] found this method to be unreliable. Dobson however obtained satisfactory results for the system ethyl alcohol-water by this method. Most investigators using the air-bubbling method have assumed very complacently that liquids produce the same vapor pressure when in contact with an inert gas as when they are in contact only with their own saturated vapor. This simplifying assumption is quite contrary to the experimental results of Campbell[8] and of Regnault. Regnault found that liquids gave values for vapor pressures by the air-bubbling method which were 1 to 2% lower than the values obtained by the static method. Campbell found that the vapor pressures of water at 70° in the presence of air was 4% low and in the presence of hydrogen 1.3% low. His results on other liquids show similar deviation.

Calingaert and Hitchcock[9] have devised a static method based upon the vapor relations of the system at equilibrium. The interferometer gives a means of determining the vapor composition in a static method, since the composition can be calulated from the refractive index. Cunaeus[10] applied this method to the system acetone-ether, but obtained unsatisfactory results which he attributed to an adsorbed film on the glass surfaces of the interferometer chamber. He concludes that only an approximate composition can be obtained by this instrument. Hoover and Glassey[11] used the interferometer for the systems methyl alcohol-water and ethyl alcohol and state that their results agree with Wrewsky's values. Bancroft and Davis point out the obvious inaccuracies in Wrewsky's data. Culbertson[12] measured the

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[1] Z. Physik. Chem., **35**, 129 (1900).

[2] Z. physik. Chem., **81**, 1 (1912).

[3] Z. physk. Chem., **68**, 641 (1909).

[4] Z. physik. Chem., **99**, 71 (1921).

[5] Ann. Chim. Phys., (3), **15**, 129 (1845)

[6] Ber. **22**, 1084 (1889).

[7] J. Phys. Chem., **1**, 753 (1897).

[8] Trans. Faraday Soc., **10**, 197 (1910).

[9] J. Am. Chem. Soc., **49**, 750 (1927).

[10] Z. physik. Chem., **36**, 232 (1901).

[11] Trans. Roy. Soc. Canada III, (3) **19**, 35 (1925).

[12] Proc. Roy. Soc., **85A**, 306 (1911).

vapor pressure of liquid bromine by the gas interferometer. Werner[1] summarizes the applications of the interferometer to gas analysis but in all these cases the gas has a very low critical temperature. Barus[2] studied the absorption of oxygen by phosphorus using an interferometer, but concluded that the instrument was too sensitive a thermometer to give accurate pressure values. Recently Morton has used the interferometer to study the systems methyl alcohol-acetone and acetone-water. The method used in the present work is similar to Morton's in principle and differs only in the details of the apparatus and manipulation.

Morton has given the equations for the calculation of the mol fraction of one component in the vapor under the special condition that the air pressure in the one chamber was adjusted to give the same refractivity as the vapor. In the procedure followed in this work, the air pressure was adjusted to give a convenient reading on the interferometer scale. The following formulae will be used.

Let n = the refractive index of a gas
R_1 = the refractivity of gas A at the pressure P_1 and absolute temperature T_1
R_2 = the refractivity of the gas B at P_2 and T_2
R_m = the refractivity of a mixture of A and B at P_m, T_m
a = the mol fraction of A in the mixture
$1-a$ = the mol fraction of B in the mixture
$R_1°$, $R_2°$, $R_m°$ = the respective refractivities at 273°A. and 760 mm. pressure (Zero refractivity)

By definition

$$R = n - 1$$

By the law of Gladstone and Dale[3]

$$\frac{n-1}{d} = \frac{R}{d} = r \qquad (6)$$

where d is the density and r is a constant, the specific refraction.
Assuming that the mixed vapors follow the gas law,

$$d = c_1 \frac{P}{T}$$

Since the refractivity is proportional to the density

$$R = c_2 \frac{P}{T}$$

To evaluate c_2 substitute $R°$ for R and the corresponding values of P and T.

$$c_2 = \frac{273}{760} R°$$

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[1] Z. angew. Chem., 38, 905 (1925).
[2] Proc. Nat. Acad. Sci., 14, 939 (1928).
[3] Phil. Trans., 1858, 887; 1863, 317.

Hence,

$$R = \frac{273\ P}{760\ T} R^\circ \tag{7}$$

and

$$R^\circ = \frac{760\ T}{273\ P} R \tag{8}$$

Assuming that in the vapor the refractivities of the two gases are additive

$$Rm^\circ = a\ R_1^\circ + (1-a)R_2^\circ$$

Solving for *a:*

$$a = \frac{R_m^\circ - R_2^\circ}{R_1^\circ - R_2^\circ} \tag{9}$$

For air, equation (7) becomes

$$R_a = \frac{273\ P}{760\ T}(0.0002917),\ R_a^\circ = 0.0002917^{1}$$

or,

$$R_a = 0.0001051\ \frac{P}{T} \tag{10}$$

In this derivation there are three points which may be questioned on the basis of their validity: (1) The law of Gladstone and Dale has been assumed to apply, (2) The gas law has been applied to mixtures of alcohol and water vapor, (3) The refractivities of the vapors in a mixture have been assumed to be additive.

The equation of Gladstone and Dale is the one to be expected if transparent substances owe their refractive power to their molecules alone and the refractivity changes proportionally with the density at all temperatures. Gale[2] summarized the other equations which have been proposed. Jamin's[3] equation:

$$\frac{n^2 - 1}{d} = \text{constant}$$

for gases is almost the same as (6),

$$\frac{n^2 - 1}{d} = \frac{(n - 1)(n + 1)}{d} = \frac{2(n - 1)}{d}$$

since (n + 1) differs very little from 2. On the basis of the electromagnetic theory of light, Lorentz[4] derived the equation,

$$\frac{n^2 - 1}{(n^2 + 2)\ d} = \text{constant}$$

This relation also mounts to practically the same as (6),

$$\frac{n^2 - 1}{(n^2 + 2)\ d} = \frac{(n - 1)(n + 1)}{(n^2 + 2)\ d} = \frac{2(n - 1)}{3d}$$

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[1] Meggers and Petters: Bur. Standards Bulletin, **14,** 698 (1918).

[2] Phys. Rev., **14,** 1 (1902).

[3] Ann. Chim. Phys., (3) **52,** 163 (1858).

[4] Wied. Ann., **9,** 641 (1880).

since for gases n^2 differs very little from unity. Gale found that air at constant temperature up to 20 atmospheres deviated not more than 0.1% from the equation of Gladstone and Dale. Posejpal[1] found that air between 0 and 760 mm. deviated by only 0.25%. This experimental work was at one temperature only. Miss Matthews[2] has reviewed the evidence on these equations and came to the same conclusion as Gale. However, there is much doubt as to whether the equation of Gladstone and Dale is valid when the temperature is varied. The evidence is equally divided and hence dependent upon the gas.

The deviation from the gas law is probably negligible for alcohol and water vapor under the experimental conditions. Kendall[3] showed that saturated steam at 100°C. follows van der Waals' equation when the values of a and b are derived from the critical data. Dobson showed that the deviation of saturated water vapor from the perfect gas-law amounts to only 0.03% at 25°C. and for alcohol the deviation was less than 0.1%. However, no data are available on the deviations of mixtures of these two vapors from the gas law.

The additivity of refractivities of gases in mixtures is the law of Biot and Arago. Ramsay and Travers[4] found that the refractivity of mixtures of hydrogen and helium deviated from the calculated value as much as 3.0%. Valentiner and Zimmer[5] observed that the dispersion of the white light amounted to 1 or 2 interference bands for hydrogen-helium mixtures. Even when the correction for dispersion was made, the calculated values for refractivity deviated by 1% on either side of the observed values. Cunaeus reported 1% deviations in mixtures of hydrogen and carbon dioxide; Valentiner and Zimmer confirmed this observation. It is doubtful if this difference can be accounted by deviations from the perfect gas.

Apparatus

A schematic representation of the interferometer apparatus for the measurement of partial pressures in the system ethyl alcohol-water at 25°C. is given in Fig. 1. The solution is contained in a 1000 cc. flask F which is surrounded by a portable thermostat constant to better than 0.01°C. The flask F is connected through the stopcock *a* (3 mm. bore) to the right-hand chamber C_2 of the interferometer and at the far end of C_2 to a mercury manometer M_2. Air free from carbon dioxide and water vapor may be introduced into either chamber of the interferometer through the calcium chloride towers T_2 and the ascarite towers T_2. The left-hand chamber C_2 is connected to the open mercury manometer M_1 which measures the pressure of the reference gas. The glass stopcocks *b*, *c*, *d*, *e* are arranged so that the flask F, C_1 and C_2 can be evacuated independently of each other.

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[1] Ann. Physik, (4), **53**, 629 (1918).

[2] J. Franklin Inst., **177**, 673 (1914).

[3] J. Am. Chem. Soc., **42**, 2481 (1920).

[4] Proc. Roy. Soc., **62**, 225 (1897).

[5] Verh. deutsch. physik. Ges., **15**, 1301 (1913).

Ordinary 9 mm. glass tubing was used for the open manometers to avoid a high meniscus. The connecting tubes were of 7 mm. tubing. The connections to the brass nipples of the interferometer chambers were made by shaping the glass to fit; then the joints were sealed by ordinary sealing wax. This avoided all rubber connections which are unreliable. The vapor from the solutions did not come in contact with the sealing wax since it merely held the joints firmly together.

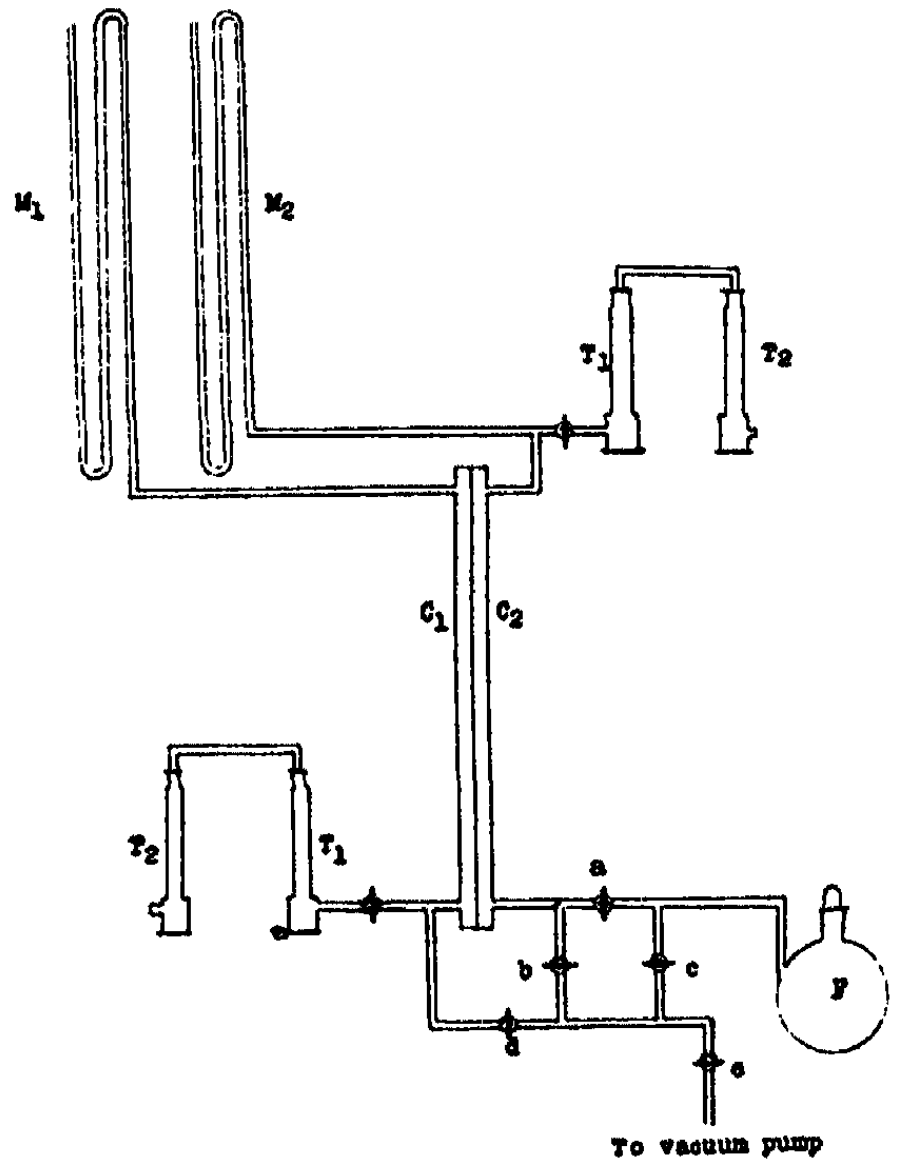

Fig. 1
Interferometer Apparatus

The interferometer was a Zeiss laboratory type with a 100 cm. chamber. This instrument is capable of measuring differences in refractivities to ± 2. $\times 10^{-7}$ and has a range of about 5 units in the fifth decimal place. The instrument was not equipped with a thermostatic bath around the chambers so that the room temperature had to be controlled.

Procedure

The interferometer must first be calibrated as it measures only differences in refractivity of the gases in the two chambers. The customary method of calibration is to place the reference gas in one chamber and determine the number of scale divisions on the compensator the interference bands are shifted when the other chamber contains the reference gas plus a known percentage of the gas which is to be determined. This gives an empirical calibration which is suitable for industrial purposes as in the determination of methane in mine gas. For the present work air free from carbon dioxide and water vapor was used as a reference gas and the instrument was calibrated by the method of Edwards.[1] For this calibration both chambers are filled with air free from carbon dioxide and water; the pressure in the one chamber is then reduced by known amounts and the corresponding compensator readings are determined. The difference in refractivity due to the difference in pressure is then calculated by the equation,

$$R = \frac{273 \times 0.0002917\,(P_1 - P_2)}{760\,T}$$

This equation is readily obtained from the previous equation (7). The pressures were measured on the manometers. One scale division was equal to 1.65 × 10^{-8} difference in refractivity.

The solutions were made up from 95% alcohol redistilled from calcium oxide. The alcohol gave no indication of fusel oil, acetone, aldehyde and oxidizable organic impurities when the appropriate tests[2] were made. The composition of the liquid was determined after each run by means of a 15 cc. Sprengel-type pycnometer, which were kept in a thermostat at 25°C. for one hour, dried and stood in balance case for a half hour before weighing. Vacuum corrections were applied and the composition calculated from the recorded densities.[3]

In each determination the solution was refluxed in an all-glass apparatus to remove a large part of the dissolved air. The solution was then cooled in the flask F by liquid air and the system evacuated by a good vacuum pump. The thermostat was brought into place and the solution held at 25 ± .01°C. for two hours while the flask was frequently shaken. To remove the last trace of air the solution was again cooled and the system evacuated to less than 0.1 mm. pressure. The thermostat was then replaced and after two hours with frequent shaking equilibrium was established. In fact, after eight hours the interferometer reading had not changed appreciably. While waiting for the solution and vapor to reach equilibrium, the zero of the instrument was checked by evacuating both chambers. Air was admitted and the evacuation repeated until the zero setting of the fringes agreed within the accuracy of the setting which is two or three scale divisions. The zero was quite constant and varied little during the entire series of experiments.

When the solution and vapor were in equilibrium, the stop-cock *a* was opened slowly so there was no sudden change in the pressure on the solution. While the vapor was flowing into C_2 the pressure in C_1 was controlled so that the the same interference bands could be kept in the field of view by turning the compensator screw. In this way it was possible to show that the

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[1] J. Am. Chem. Soc., **39**, 2382 (1917).

[2] Murray: "Standards and Tests for Reagents and Chemicals," 78 (1927).

[3] "International Critical Tables," **3**, 116.

same two bands used in the zero reading were used in the reading with the vapor. The chromatic dispersion observed by Valentiner and Zimmer is not observable in the case of alcohol and water vapors. The vapor was kept in the chamber for one half hour before the final reading was taken. This allowed the vapor to come to room temperature (28°C.). All readings were taken at this temperature which was high enough to prevent any detectable condensation.

The first interferometer readings were generally a little low, but the final values were taken on separate samples of the vapor which agreed within 5-10 scale divisions. At the same time the interferometer was read, the mercury manometers were measured with a cathetometer accurate to 0.1 mm. A barometer in the same room was also read. All pressures were corrected for temperature and recorded in millimeters of mercury at 0°C. The difference between barometric pressure and the reading on M_2 is the total pressure of the solution (P_m). The difference between barometric pressure and the reading on M_1 is the pressure of the air and is substituted into equation (10) which gives the refractivity of the air under the experimental conditions. The interferometer reading is multiplied by 1.65×10^{-8} and added to R_a to obtain the refractivity of the vapor under the experimental conditions. The zero refractivity of the vapor is then calculated by means of equation (8); the mol fraction of alcohol in the vapor is obtained from equation (9). The partial pressures of alcohol P_a and of water P_w are readily obtained from the relations,

$$P_a = a\,P_m$$
$$P_w = P_m - P_a$$

Absolute alcohol redistilled from calcium oxide was used for the determination of the vapor pressure and refractivity of pure alcohol. It contained less than 0.1% water by the density determination. The value for the zero refractivity of alcohol was 0.000886 which agrees well with the recorded values[1] 0.000871 and 0.000885 for sodium light. The vapor pressure of ethyl alcohol was 58.8 mm. which is very good considering that it contained a little water. The recorded vapor pressure[2] of ethyl alcohol at 25° is 59.0 mm. The zero refractivity of water was 0.000257 which agrees with Morton's value and the recorded values[1] which are respectively 0.000255 and 0.000257. The vapor pressure of water was 23.7 as against 23.76 the recorded value.[3]

The interferometer cannot be applied equally well to all binary systems. Equation (9) shows that to be applicable the two components must have refractive indices which are quite different. The difference in the case of ethyl alcohol vapor and water vapor is 0.000629 so that the maximum accuracy considering only the vapor composition is about 1 part in 600. The manometer readings enter into the calculation of the mol fraction. If the error on the pressure is taken as 0.1 mm. and the average total pressure as

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[1] "Landolt-Börnstein," 2, 961.

[2] "International Critical Tables," 3, 217.

[3] "International Critical Tables," 2, 212.

40 mm. the accuracy obtained is about 1 in 400. The mol fraction of ethyl alcohol in the vapor recorded is the average of two or more values agreeing to 1. part in 500. The analysis of the liquid is accurate to 0.1%. The values obtained are dependent upon several factors which are not readily evaluated, namely: the validity of the law of Gladstone and Dale at varying temperatures, the additive nature of refractivities of the vapors, and the presence of an adsorped layer of the vapors on the glass ends of the interferometer chamber. The results of the interferometer method are summarized in Table I.

The distillation experiments were carried out in an all-glass apparatus which consisted of a 1000 cc. flask and a 50 cc. receiver both connected to a 7 mm. delivery tube by ground-glass joints. The delivery tube contained a

TABLE I

Vapor Pressures of Alcohol-Water Solutions at 25°C.

Percent alcohol in Solution	Total vapor pressure P_m mm.	Zero refract. of vapor $R_m^\circ \times 10^{-6}$	Mol fraction alcohol in vapor a	Partial pressure alcohol P_a' mm.	Partial pressure water P_w' mm.	Total vapor pressure Dobson mm.
0	23.7	257	0	0	23.7	—
5.30	27.9	489	0.369	10.3	17.6	28.2
13.74	34.2	617	.573	19.6	14.6	34.2
25.32	41.2	680	.673	27.7	13.5	41.5
34.38	45.6	701	.705	32.2	13.4	45.9
46.21	48.7	714	.727	35.4	13.3	48.8
54.85	50.6	726	.746	37.7	12.9	50.9
65.53	52.5	742	.772	40.5	12.0	52.7
75.25	54.4	757	.796	43.3	11.1	55.0
84.79	56.1	774	.822	46.1	10.0	56.9
92.30	58.4	803	.869	50.7	7.7	58.3
94.96	57.8	827	.906	52.4	5.4	58.5
100.0	58.8	886	1.000	58.8	0	59.0

TABLE II

Weight % in Soln.	Alcohol in vapor	Mol. Frac. vapor	Total P_m	Partial P_a'	Pressures P_w'
26.37	69.66	.474	41.8	19.8	22.0
33.29	74.30	.531	45.2	24.0	21.2
42.58	76.62	.562	47.9	26.9	21.0
54.70	78.03	.582	50.7	29.6	21.1
56.54	78.55	.589	51.0	30.1	20.9
66.48	80.64	.620	52.7	32.7	20.0
66.79	80.56	.619	52.8	32.7	20.1
77.87	84.80	.685	54.8	37.6	17.2
92.55	93.50	.849	58.4	49.6	8.8

three-way stopcock for evacuating the system. A thermostat held the temperature of the solution constant at 25 ± .01° during the distillation.

The solutions were made up as in the previous experiments and the air removed by evacuating. The receiver was surrounded by thermostat and 15 cc. of the distillate were collected while the flask was shaken frequently. Since 500 cc. of solution used for each distillation, the composition of the liquid phase remained practically constant during the distillation. The solution and distillate were analyzed by the density method as in the previous procedure. The total pressures obtained in the interferometer method were used to calculate the partial pressures. The results of the distillation experiments are summarized in Table II.

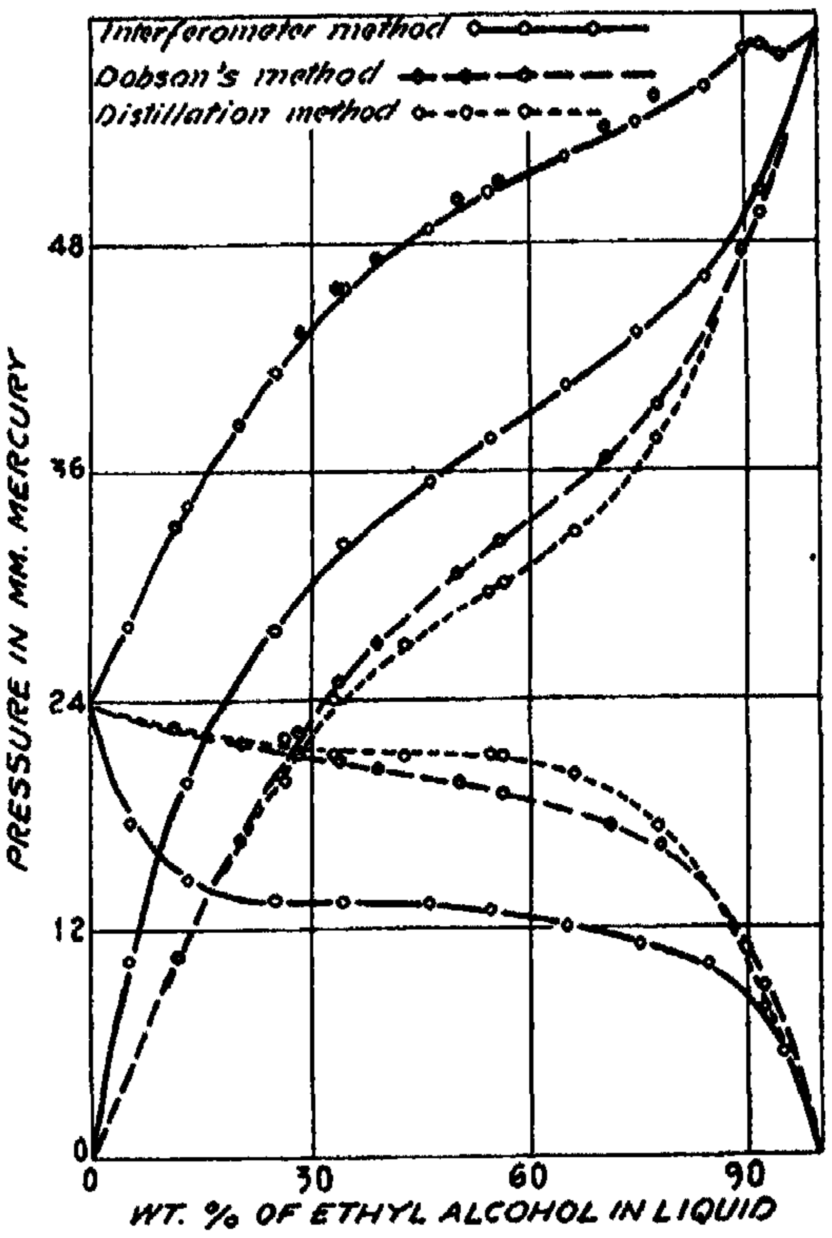

FIG. 2
Total and Partial Pressures for the System Ethyl Alcohol-Water at 25°.

Discussion

The data on the partial pressures in the system ethyl-alcohol-water at 25°C. by three methods (bubbling method, distillation and interferometer method) are plotted in Fig. 2. A comparison can be made most readily by means of this diagram. The total pressures by the static and dynamic methods agree very well up to a concentration of 40% alcohol; above this concentration Dobson's values are slightly higher. If air raises the vapor pressure of the solution in this range, the difference is readily explained; however, Campbell's results show that air lowers the vapor pressure of pure alcohol and of water also. One would expect the partial pressures from a solution of the two to be lowered also. It may be that this difference is due to a systematic error in the dynamic method since pressure is not measured directly in that procedure. The differences are larger than the experimental error in the static method.

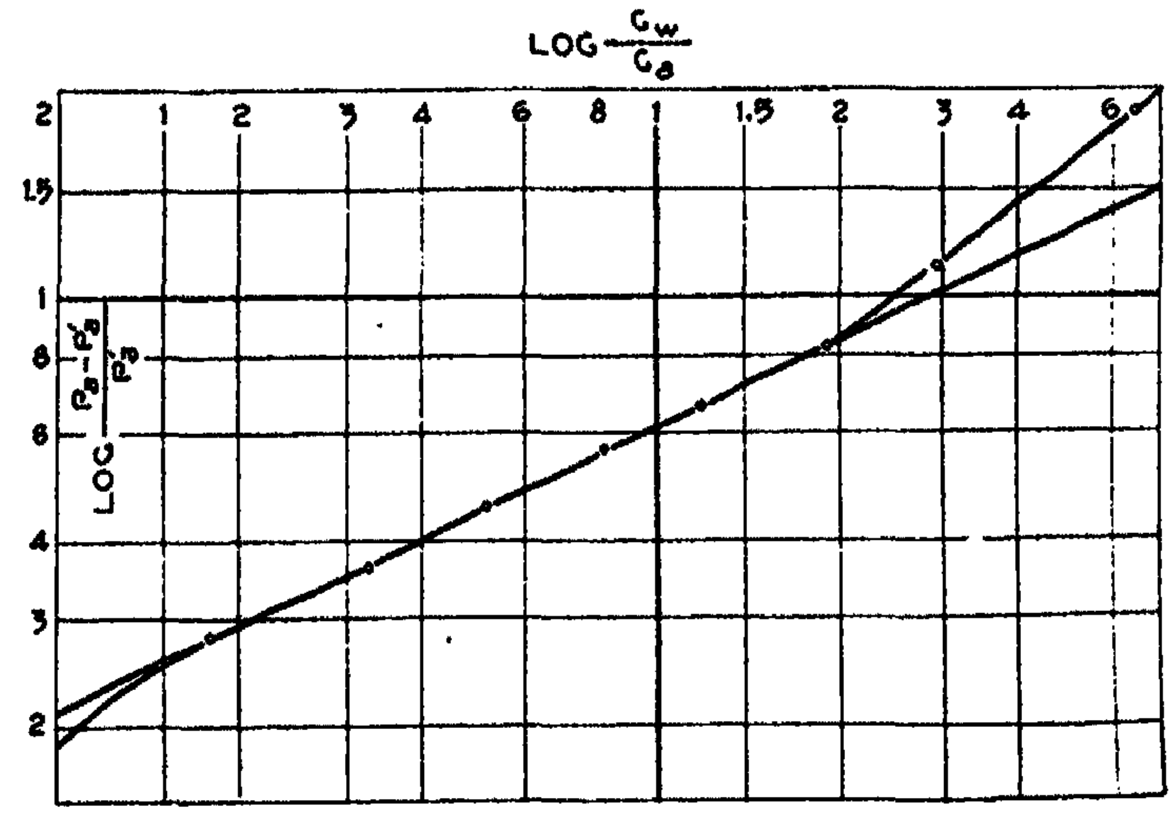

Fig. 3

Ethyl Alcohol and Water at 25°.

Equation for Partial Pressures of Ethyl Alcohol $0.463 \log G_w/G_a - \log \frac{P_a - P'_a}{P'_a} = 0.210$

The partial pressure curves for water and alcohol by the distillation method are respectively above and below the corresponding curves by Dobson. The lower partial pressures of water by the dynamic method may be due to the presence of air, but in that case the partial pressure of alcohol should also be lower. This may mean that air lowers the partial pressure of water but raises that of alcohol in such a way that the total pressure is only raised slightly. No data are available to show the effect of an inert gas upon the partial pressures from a solution. The distillation experiments were merely intended to show whether the interferometer values or Dobson's values were in error. With a distillation method it is difficult to decide whether the vapor distilling is always in equilibrium with the solution, although the duplicate determinations agree.

There is very nearly a constant difference between the partial pressures by the interferometer and those by the distillation and by Dobson's procedure. This probably means a systematic error in the interferometer method.

If an adsorbed gas layer is formed on the glass plates of the interferometer chamber, a high value for the refractivity of the vapor would be obtained and hence a larger apparent mol fraction of alcohol in the vapor. This effect is in the right direction to account for the differences between the interferometer values and the values by the other two methods. Cunaeus calculated the thickness of the adsorbed film which must be formed to account for the deviations in the system acetone-ether. He found that the film was of the same order of magnitude as observed by Müller-Erzbach[1] for adsorbed gas layers on solids. A second uncertainty in the interferometer procedure is the additive nature of refractivities of the vapors. The only experimental work on this was done on gas with very low critical temperatures and in these cases large deviations were observed. The results show that if the interferometer is to be used for the determination of partial pressures a strictly empirical method must be used. Synthetic mixtures of the vapors must be made and their refractivities determined. Time was not available for carrying out this method.

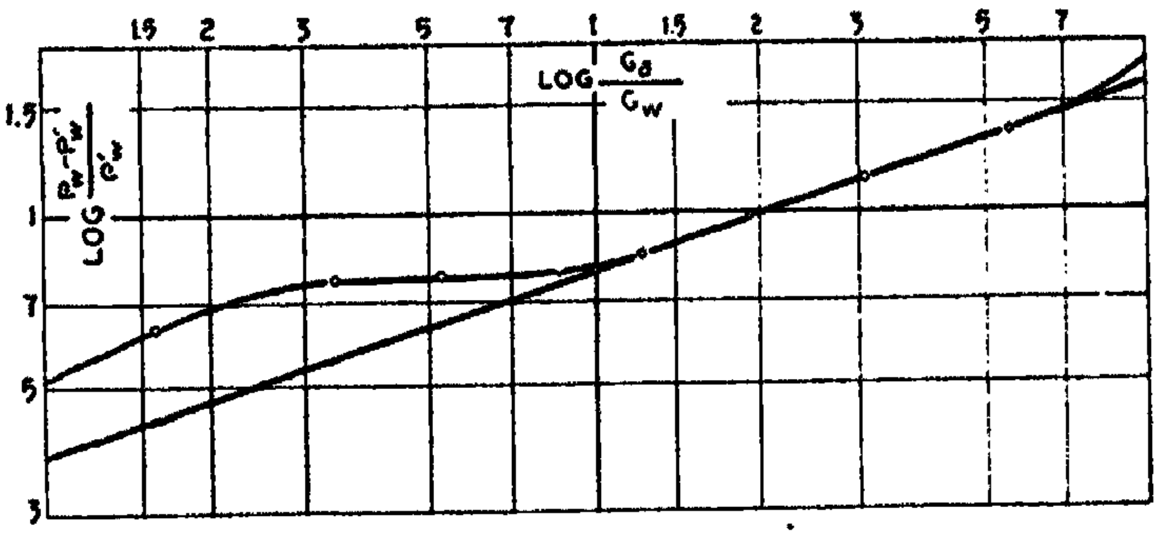

Fig. 4

Ethyl Alcohol and Water at 25°

Equation for Partial Pressures of Water $0.332 \log G_a/G_w - \log \frac{P_w - P'_w}{P'_w} = 0.099$.

The results of the interferometer method were substituted into equation (5) and the partial pressures calculated; the results are shown in Table III. The logarithmic graphs for water and alcohol are shown in Figs. 3 and 4. The calculated partial pressures agree fairly well with the experimental values from 20 to 90% alcohol in the solution. The equation is very difficult to apply to the data on water since the percentage error is very large and is magnified by the pressure term in the equation.

Equation (5) has been applied to the system benzene-carbon disulphide at 20, 25 and 30°C. using the data by Sameshima.[2] The calculated and experital results at these temperatures are shown respectively in Tables IV, V and VI. At 20°C. the average deviation of the calculated values amounts to only

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[1] Wied. Ann., 25, 357 (1885).

[2] J. Am. Chem. Soc., 40, 1504 (1918).

2 or 3 parts in 500 except in the case of the 87.8 mol percent solution where a 25% deviation occurs for carbon disulphide. It is probable that this point is in error since there is a slight hump in the curve at this point.

The calculated values for benzene in carbon disulphide at 25° (Table IV) agree beautifully with the experimental data from 5 through 95 mol percent.

TABLE III
Ethyl Alcohol—Water at 25°C.

$$0.322 \log \frac{G_a}{G_w} - \log \frac{P_w - P_w'}{P_w'} = \log K_1 = 0.099$$

$$0.463 \log \frac{G_w}{G_a} - \log \frac{P_a - P_a'}{P_a'} = \log K_2 = 0.210$$

Wt. % Alcohol in solution	Log K_1 Calcd.	P_w' Exp. mm.	P_w' Calcd. mm.	Log K_2 Calcd.	P_a' Exp. mm.	P_a' Calcd. mm.
0	—	23.7	—	—	0	—
5.30	0.0504	17.6	18.1	−0.0955	10.3	17.7
13.74	−.0565	14.6	16.5	+.0660	19.6	21.0
25.32	−.0338	13.5	15.2	.1644	27.7	29.2
34.38	.0197	13.4	14.5	.2101	32.2	32.2
46.21	.0811	13.3	13.5	.2065	35.4	35.4
54.85	.1003	12.9	12.9	.2088	37.7	37.7
65.53	.0972	12.0	12.0	.2110	40.5	40.5
75.25	.0975	11.1	11.1	.2172	43.3	43.1
84.79	.1003	10.0	10.0	.2075	46.1	46.1
92.30	.0275	7.7	8.6	.2869	50.7	49.4
94.96	−.1221	5.4	7.8	.3088	52.4	50.5
100.0	—	0	—	—	58.8	—

TABLE IV
Benzene-Carbon Disulphide at 20°C.

$$0.860 \log \frac{N_c}{N_b} - \log \frac{P_b' - P_b'}{P_b'} = \log K_1 = 0.108$$

$$0.883 \log \frac{N_b}{N_c} - \log \frac{P_c - P_c'}{P_c'} = \log K_2 = 0.098$$

Mol % Benzene Soln.	log K_1 Calcd.	Benzene P_b' Exp. mm.	log K_2 Calcd. mm.	Calcd.	Carbon Disulphide P_c' Exp. mm.	Carbon Disulphide P_c' Calcd. mm.
0	—	0	—	—	297.4	—
11.35	0.1040	13.4	13.5	0.1068	263.8	263.0
24.82	.1217	25.4	24.9	.0920	228.1	228.6
37.47	.1094	34.0	34.0	.1061	198.4	197.4
46.24	.1093	39.9	39.9	.1031	175.8	175.2
62.51	.1147	50.3	50.0	.0954	131.6	132.0
87.80	.2502	68.2	65.8	.0210	42.5	53.5
100.00	—	75.2	—	—	0	—

TABLE V

Benzene—Carbon Disulphide at 25°C.

$$0.908 \log \frac{N_c}{N_b} - \log \frac{P_b - P_b'}{P'_o} = \log K_1 = 0.112$$

$$0.924 \log \frac{N_b}{N_c} - \log \frac{P_c - P_c'}{P_c'} = \log K_2 = 0.090$$

Mol % Benzene Soln.	log K_1 Calcd.	P_b' Benzene		log K_2 Calcd.	P_c' Carbon Disulphide	
		Exp.	Calcd.		Exp.	Calcd.
0	—	—	—	—	361.1	—
2.11	0.0974	3.5	2.7	0.0984	352.7	352.4
4.68	.1135	7.1	7.4	.1183	344.1	343.8
11.53	.1102	16.0	16.0	.0908	321.4	321.3
18.24	.1209	24.0	23.6	.0817	299.1	299.6
18.86	.1097	24.2	24.3	.0883	297.9	298.1
30.02	.1028	35.1	35.5	.0912	263.6	263.6
43.88	.1111	48.2	48.2	.0872	218.7	219.3
49.86	.1178	53.7	53.4	.0783	197.4	200.0
57.38	.1154	59.8	59.6	.0857	173.8	174.3
63.02	.0946	63.5	64.3	.0971	156.6	155.0
76.63	.1167	75.3	75.1	.0747	102.5	105.0
87.14	.1232	83.8	83.6	.0690	60.2	62.5
94.19	.1233	89.5	89.4	.0419	27.9	33.8
100.00	—	94.9	—	—	0	—

TABLE VI

Benzene—Carbon Disulphide at 30°C.

$$0.883 \log \frac{N_c}{N_b} - \log \frac{P_b - P_b'}{P_b'} = \log K_1 = 0.092$$

$$0.915 \log \frac{N_b}{N_c} - \log \frac{P_c - P_c'}{P'_c} = \log K_2 = 0.085$$

Mol % Benzene Soln.	log K_1 Calcd.	P_b' Benzene		log K_2 Calcd.	P_c' Carbon Disulphide	
		Exp. mm.	Calcd. mm.		Exp. mm.	Calcd. mm.
0	—	0	—	—	434.6	—
8.00	0.0861	14.7	14.9	0.0707	398.4	399.8
22.86	.0990	35.8	36.1	.0902	343.1	342.0
37.23	.1066	53.3	52.4	.0846	287.5	287.5
65.16	.0956	81.6	81.6	.0873	177.5	176.7
88.45	.1713	107.3	105.2	.0311	62.2	69.0
100.00	—	119.3	—	—	0	—

For solutions beyond these limits the equation magnifies the error enormously. The values for the partial pressure of carbon disulphide tend to deviate increasingly when the mol percent exceed 63. The agreement is very good except in the case of about four solutions. The calculated values for this system at 30° (Taple VI) agree with the experimental data very well except at 88 mole percent where a large deviation occurs. It is believed that this value would lie on the straight of equation if more data were available at this temperature. It is quite evident that equation (5) represents the experimental facts adequately for this sytem.

Most investigators in studying binary mixtures of non-electrolytes have confined their attention to mixtures of two volatile components. The simplest case is obviously that of two normal liquids of which only one is measurably volatile at the temperature of the experiments. In this case a static method can be used and the procedure is quite simple. It is surprising that only a few systems of this type have been investigated: the only data are those by Campbell and by Foote and Dixon.[1] It was thought to be worth while to apply equation (5) to this case although the data are not of highest possible accuracy in certain cases.

Campbell has investigated all possible combinations of normal and associated liquids forming a binary mixture with one volatile component. The following are the combinations to be considered:

1. Both normal
    - Oleic acid and ether 30° (VII)
    - Oleic acid and carbon disulphide 30° (VIII)
2. Normal non-volatile liquid with an associated volatile liquid
    - Oleic acid and acetone 30° (IX)
3. An associated non-volatile liquid with a normal volatile liquid

TABLE VII

Ether—Oleic Acid at 30°C.

$$0.992 \log \frac{G_o}{G_e} - \log \frac{P_e - P_e'}{P_e'} = \log K = 0.484$$

Wt. % Ether Soln.	P_e' Ether Pressure Exp. mm.	P_e' Ether Pressure Calcd. mm.	log K Calcd.
4.96	96.7	90.0	0.5207
7.17	119.9	124.2	.4648
14.36	217.9	219.1	.4793
23.55	303.7	312.5	.4607
37.40	414.8	415.0	.4829
61.93	535.6	534.0	.4916
100.0	642.1	—	—

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[1] Am. J. Sci., 17, 146 (1929).

TABLE VIII

Carbon Disulphide—Oleic Acid at 30°C.

$$1.143 \log \frac{G_o}{G_c} - \log \frac{P_c - P_c'}{P_c'} = \log K = 0.626$$

Wt % CS₂ Soln.	Carbon Disulphide Exp. mm.	Calcd. mm.	log K Calcd.
3.12	40.9	33.2	0.7252
15.75	164.0	165.7	.6191
25.85	233.7	242.0	.5937
34.77	290.5	291.0	.6258
40.51	316.3	316.4	.6279
56.14	366.6	366.6	.6270
100.0	431.9	—	—

TABLE IX

Acetone—Oleic Acid at 30°C.

$$0.974 \log \frac{G_o}{G_a} - \log \frac{P_a - P_a'}{P_a'} = \log K = 0.817$$

Wt. % Acetone Soln.	P_a' Acetone Pressure Exp. mm.	Calcd. mm.	log K Calcd.
2.79	48.7	47.0	0.8373
11.99	130.6	133.8	.7973
20.76	180.0	179.7	.8207
37.60	220.4	220.5	.8142
100.0	275.8	—	—

TABLE X

Ether—Sulphuric Acid at 30°C.

$$2.85 \log \frac{G_s}{G_e} - \log \frac{P_e - P_e'}{P_e'} = \log K = -0.595$$

Wt. % Ether Soln.	E Ether Exp. mm.	P_e' Pressure Calcd. mm.	log K. Calcd.
41.59	34.8	56.8	−0.8246
54.51	192.2	191.6	.5924
56.35	229.7	220.7	.5687
68.76	455.1	455.1	.6066
76.90	554.4	570.0	.6873
97.13	631.8	642.0	2.6572
100.0	642.1	—	—

TABLE XI

Methyl Alcohol—Glycerol at 40°C.

$$1.042 \log \frac{G_g}{G_a} - \log \frac{P_a - P_a'}{P_a'} = \log K = 0.747$$

Wt. % Alcohol Soln.	Methyl Alcohol Pressure		log K Calcd.
	Exp. mm.	Calcd. mm.	
6.26	62.1	64.0	0.7302
8.55	83.8	82.7	.7563
18.33	137.5	138.4	.7403
25.53	167.1	166.3	.7523
38.28	199.6	198.6	.7540
56.27	222.9	226.0	.6961
83.68	244.8	248.3	.5483
100.0	257.4	—	—

TABLE XII

Water—Glycerol at 70°C.

$$1.107 \log \frac{N_g}{N_w} - \log \frac{P_w - P_w'}{P_w'} = \log K = -0.108$$

Mol % Water Soln.	P_w' Water Pressure		Log K Calcd.
	Exp. mm.	Calcd. mm.	
41.0	79.8	80.2	−0.1110
59.9	128.1	128.1	.1089
76.4	173.4	173.2	.1060
86.2	199.9	200.0	.1106
94.9	222.3	222.2	.1192
97.4	229.3	228.2	.0340
97.7	230.9	229.0	.1031
100.0	233.8	—	—

Sulphuric acid and ether 30° (X)

4. Both associated
    - Glycerol and methyl alcohol 40°C (XI)
    - Glycerol and water 70°C (XII)

The data of Campbell for all these cases have been used except for glycerol and water in which case the data are by Perman and Price.[1] The Roman numeral after the sytems listed above refers to the table in which the calculated and experimental values of the partial pressures are given. Campbell measured the vapor pressures in the presence of hydrogen; he had previously shown that the lowering of the vapor pressure of the pure liquids on

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[1] Trans. Faraday Soc., 8, 68 (1912).

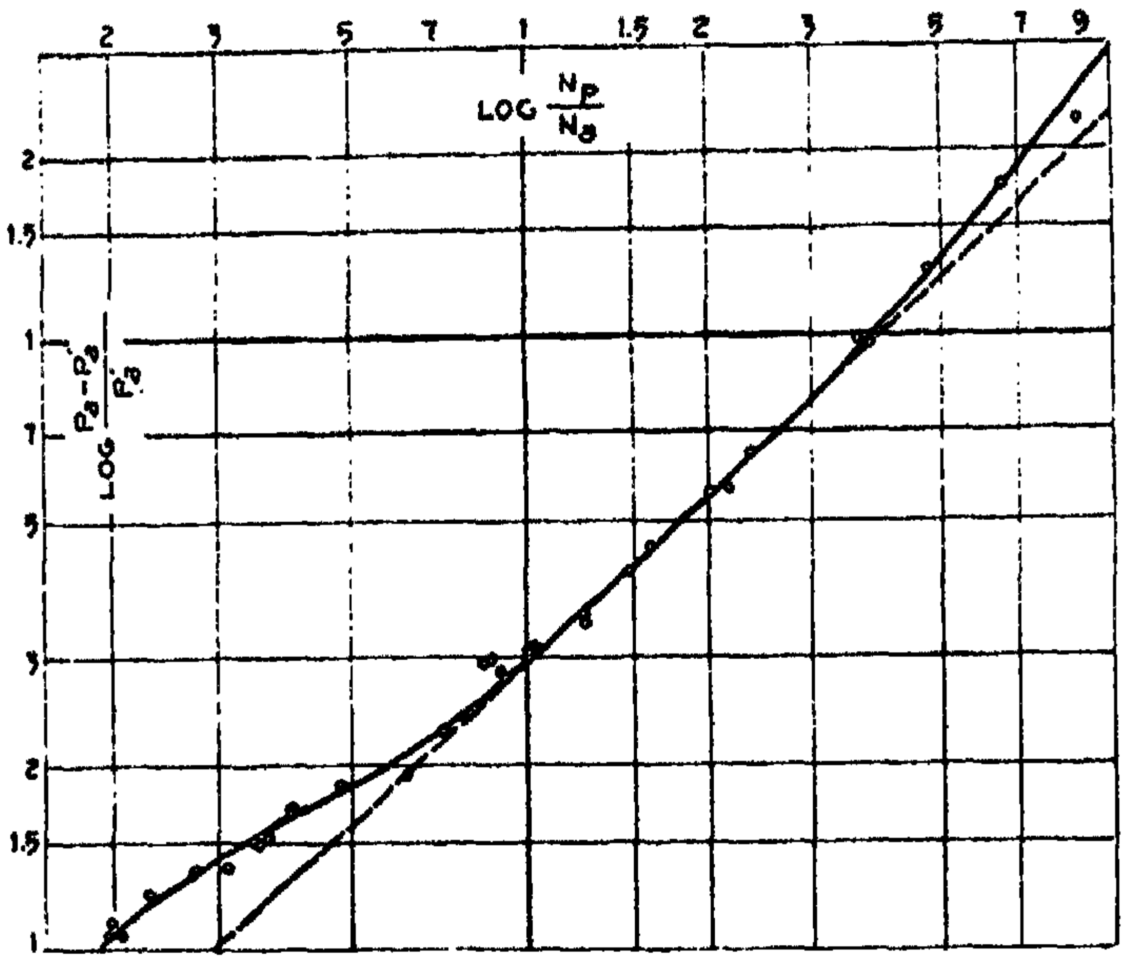

FIG. 5
Diethyl Phthalate and Ethyl Alcohol at 25°.
Equation for Partial Pressures of Ethyl Alcohol $0.882 \log N_p/N_a - \log \frac{P_a - P'_a}{P'_a} = 0.528$.

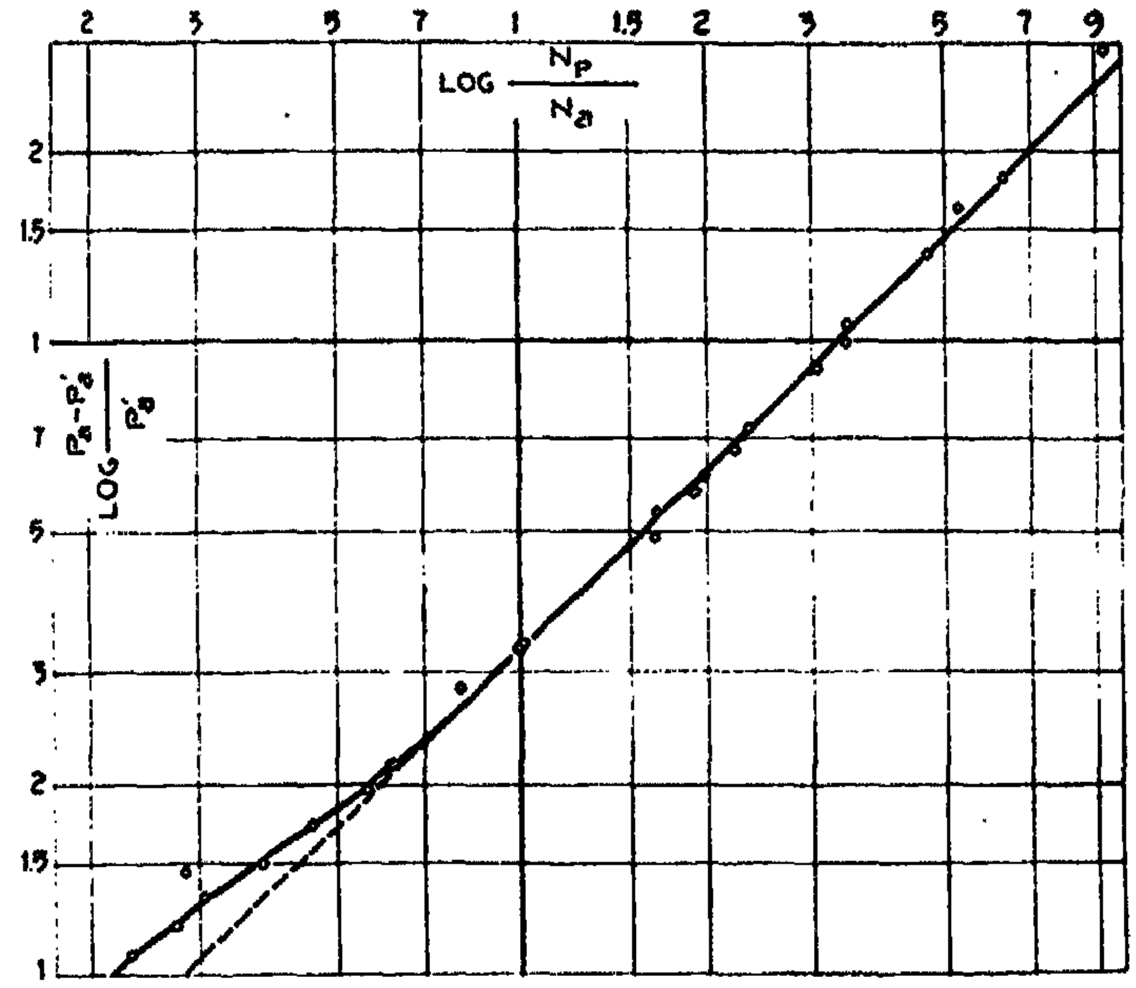

FIG. 6
Diethyl Phthalate and Methyl Alcohol at 25°.
Equation for Partial Pressures of Methyl Alcohol $0.922 \log N_p/N_a - \log \frac{P_a - P'_a}{P'_a} = 0.487$.

these conditions was: ether 0.89%, carbon disulphide 0.61%, acetone 1.85%, methyl alcohol 0.82% and water 1.28%. The agreement between the calculated partial pressures and the found values can not be expected to be any closer than the above percent.

The pressures calculated for ether in oleic acid (Table VIII) agree as well as can be expected. The value at 23.55% should be closer since the deviation at the lower concentrations is several times smaller. The values for carbon disulphide in oleic acid (Table VIII) are much better and agree within 1% except in the case of 25.85% and 3.12% solutions. The experimental value at 25.85% is very probably in error.

For an associated liquid in a non-volatile normal liquid, acetone in oleic acid (Table IX), the equation gives the vapor pressure of acetone within 1.85% of the values found. In this case the hydrogen may produce an effect as large as 1.85%. The values for ether in sulphuric acid are very erratic (Table X) which may be due to compound formation as Campbell points out. A better choice for this case could undoubtedly be made.

TABLE XIII

Diethyl Phthalate—Ethyl Alcohol at 25°C.

$$0.882 \log \frac{N_p}{N_a} - \log \frac{P_a - P_a'}{P_a'} = \log K = 0.528$$

Mol % Alcohol Soln.	P_a' Alcohol Pressure Exp. mm.	Calcd. mm.	Deviation mm.	Mol % Alcohol Soln.	P_a' Alcohol Pressure Exp. mm.	Calcd. mm.	Deviation mm.
100.0	58.8	—	—	—	45.4*	46.8	1.4
90.5	54.9	56.5	1.6	53.9	45.3*	46.7	1.4
88.6	54.4	56.0	1.5	52.7	46.3	46.3	0.0
87.5	54.3	55.8	1.5	49.2	44.8	45.0	0.2
86.6	54.1	55.6	1.5	44.5	43.4	43.3	−0.1
86.1	53.6	55.5	1.9	44.3	43.7*	43.0	−0.7
85.2	53.8*	55.3	1.5	40.1	41.5	41.4	−0.1
83.6	53.1	54.9	1.8	38.4	40.4	40.5	0.1
83.4	52.9	54.8	1.9	33.0	37.7	37.8	0.1
82.8	53.1*	54.7	1.6	31.5	37.6	37.0	−0.6
81.2	52.3	54.3	2.0	29.6	35.7	36.0	0.3
78.5	51.7	53.7	2.0	21.6	29.7*	30.5	0.8
76.2	51.6	53.2	1.6	20.7	29.9	29.1	−0.8
73.9	51.1	52.7	1.6	17.3	25.9	27.0	1.1
73.1	50.9	52.3	1.4	13.5	21.4	22.2	0.8
71.4	50.2	51.9	1.7	10.1	16.7	19.3	2.6
67.7	50.5*	50.9	0.4	7.25	13.0	15.4	2.4
67.5	49.8	50.9	1.1	6.40	11.6	14.1	2.5
61.3	49.1	49.1	0.0	3.70	6.3	9.4	3.1
58.0	47.8	48.0	0.2				

* It is evident that these values are in error.

The values for the pressure of methyl alcohol from glycerol solutions (Table XI) have a maximum deviation of 2% and the majority agree within 1%. This is very satisfactory agreement since the hydrogen can produce an 0.8% effect. The calculated values for water in glycerol (Table XII) are very satisfactory; the maximum deviation is about 0.5% and the average deviation is much less. These data were obtained by Perman and Price and are believed to be more accurate.

Quite recently Foote and Dixon[1] published data on the vapor pressure of ethyl and methyl alcohol from solutions in diethyl phthalate at 25°C. The experimental and calculated pressures are given in Tables XIII and XIV and are plotted in Figs. 5 and 6. The calculated pressures were made using the graphically determined value for K; in all previous cases K was determined mathematically for each concentration and averaged. Less deviations would be obtained if the average value for K is used, since the deviations are all in the same direction.

TABLE XIV

Diethyl Phthalate—Methyl Alcohol at 25°C.

$$0.922 \log \frac{N_p}{N_a} - \log \frac{P - P_a'}{P_a'} = \log K = 0.487$$

Mol % Alcohol Soln.	P_a' Alcohol Exp. mm.	Pressure Calcd. mm.	Deviation mm.
100.0	126.1	—	—
90.7	119.1	121.2	2.1
90.0	118.6	120.8	2.2
88.3	117.5	119.8	2.3
87.5	116.5	119.4	2.9
84.8	115.9	118.2	2.3
81.0	113.8	116.0	2.2
80.7	112.9	115.9	3.0
78.4	112.6	114.5	2.9
77.8	111.0*	114.1	3.1
76.4	111.1	113.4	2.3
72.2	109.5	111.1	1.6
68.3	107.5	108.5	1.0
64.0	105.3	105.9	0.6
61.7	103.9	104.2	0.3
55.5	98.3	99.6	1.3
49.9	95.1	95.1	0.0
49.5	94.6	94.6	0.0
37.5	84.8*	82.9	−1.9
37.3	81.9	82.7	0.8
34.1	80.0	79.0	−1.0
33.5	78.4	78.2	−0.2
30.9	75.8	74.9	−0.9
30.4	74.7*	73.5	−1.2
30.4	73.5	73.5	0.0
29.7	73.0	73.2	0.2
24.5	66.5	65.8	−0.7
22.4	63.4*	62.3	−1.1
22.4	61.3*	62.3	1.0
17.4	53.2	53.2	0.0
15.8	48.0	50.0	2.0
13.7	44.3	45.4	1.1
9.63	32.4	35.3	2.9
9.00	31.7	33.6	1.9
5.50	21.3	24.1	2.8

* It is evident that these values are in error.

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[1] Am. J. Sci., 17, 146 (1929).

Summary

1. The equation

$$a \log \frac{G_1}{G_2} - \log \frac{P_2 - P'_2}{P_2'} = \log K$$

has been shown to apply to binary systems of one volatile component over a very large range of concentrations for all combinations of normal and associated liquids. This equation represents the system benzene-carbon sulphide remarkably well at three different temperatures. The data for the system ethyl alcohol-water at 25°C. by two different methods is represented by this equation over a wide range of concentrations.

2. The interferometer method for the determination of partial pressures is unreliable unless an entirely empirical calibration is used.

Acknowledgment

This research was suggested by Professor Wilder D. Bancroft, under whose direction it has been carried out. I wish to express my appreciation of the encouraging suggestions and helpful criticisms which I have received from Professor Bancroft. I am indebted to Mr. D. S. Morton for suggestions in regard to the interferometer.

Cornell University.

THE SIGNIFICANCE OF THE HYDROGEN CONTENT OF CHARCOALS

BY H. H. LOWRY

Most studies of the thermal decomposition of hydrocarbons are confined to an examination of the composition of the liquid and gaseous products. Among exceptions to this generalization may be mentioned the interest in coke, carbon black, and charcoal. Even in these cases the physical properties rather than the chemical composition are regarded as the factors which determine their suitability for specific uses. However, in an earlier paper[1] it was pointed out that certain physical properties of a group of charcoals were rather simply related to the percent hydrogen which was contained in them as determined by ultimate analysis. This group of charcoals was prepared in a gas-fired furnace from a single, specially-selected lot of anthracite coal. As stated in this earlier paper, careful consideration of the commercial records taken at the time of preparation indicated that the hydrogen content was probably determined by the maximum temperature to which the samples were heated during their preparation. The hydrogen contents ranged from 0.21 to 0.53%, while the probable range of maximum temperature was 900° to 1200°. The presence of hydrogen in these charcoals was shown to be consistent with a point of view that so-called "amorphous" carbons are hydrocarbons of low hydrogen content[2] built up of polymerized residues from the thermal decomposition of hydrocarbons of greater hydrogen content. Since the significance of the hydrogen content of charcoals has been generally overlooked, the present study was undertaken in order to evaluate the factors which may ordinarily be varied in the preparation of charcoals for various purposes. The factors which were independently varied in this study were the maximum temperature, the time of heating, the atmosphere surrounding the sample during heating and the raw material. To a limited extent the effect of previous heat treatment was also determined. A later paper will give the results of the study of the correlation of hydrogen content and some adsorptive properties of charcoals prepared under carefully controlled conditions.

Preparation of Samples and Method of Analysis

Since the samples which are considered in this report were not all prepared specifically for this investigation, the method of preparation of certain series of samples differed from the method used in other series. In general, however, the samples were all originally ground and sifted to 60-80 mesh and heated in a controlled atmosphere for a known length of time. In all cases,

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[1] J. Am. Chem. Soc., **46**, 824 (1924).

[2] For instance, see Bancroft: J. Phys. Chem., **24**, 127 (1920); Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," page 569 (1923).

the furnace was an electric furnace of large heat capacity, heated by a platinum rhodium resistor which was so wound that for a length of about 5″ there were no temperature differences of more than ±2°. The temperature was maintained constant at the desired temperature by means of a Wheatstone bridge controller[1] specially designed with a recorder by Leeds and Northrup Company. With this controller the temperature fluctuations were reduced to less than 5° for periods extending to a week when the maximum temperature did not exceed about 1300°, above which temperature the volatilization of the platinum caused a gradual drift in temperature downwards requiring frequent manual adjustment. Except when the effect of the surrounding atmosphere on the hydrogen content was being studied, a pure dry hydrogen atmosphere was maintained. In general, the sample ranging in size from 5 grams to 50 grams was placed in a small graphite crucible which in turn was placed in the zone of maximum temperature. Temperature readings taken every 5 minutes showed that the furnace had recovered its temperature equilibrium within the first 5 minutes. At the end of the period of heating the crucible was withdrawn to a cool part of the furnace and left in the current of hydrogen until sufficiently cold to handle freely.

The hydrogen content was ascertained by means of a simple organic combustion, by which carbon was determined as carbon dioxide by absorption by soda-lime and hydrogen as water by absorption by phosphorus pentoxide. Since our earlier data indicated that the hydrogen was directly associated with the carbon and not with impurities contained therein, all analyses were calculated to an ash-free basis. In order to avoid errors in the analyses due to absorbed gas and moisture, the samples were evacuated at 200° for 6 hours and burned in a current of pure oxygen without transfer from the vessel in which they were evacuated. In this case it was unnecessary to weigh the original samples since our only interest was in the carbon and hydrogen present in the sample and these were directly determined as oxides in the analyses. Duplicate analyses on the same sample checked in the great majority of cases to within 0.02% hydrogen; if not, further analyses were made until the probable error of the average was less than 0.02% hydrogen

An alternative method developed by Mr. W. B. Warren of these Laboratories was used for certain samples having hydrogen contents less than 0.20%. This method consisted in carrying out the combustion in a closed system in which the sample could first be outgassed and which was provided with suitable fractionating traps so that the carbon dioxide could be measured volumetrically and the water weighed by absorption by phosphorus pentoxide. The weighing procedure was simply an observation by means of a cathetometer of the extension of a quartz-fiber spiral balance[2] from which was suspended a small tray of phosphorus pentoxide. The quartz-fiber balance was contained in the closed system in which the combustion took place. This

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[1] See H. S. Roberts: J. Wash. Acad. Sci., 11, 401 (1921); E. N. Bunting: J. Am. Ceramic Soc., 6, 1209 (1923).

[2] J. W. McBain and A. M. Bakr: J. Am. Chem. Soc., 48, 690 (1926).

TABLE I

Calculated and Observed Values of Hydrogen Content for Coal #1

Temp. °C	Time in Hours	Hydrogen Content %				
		Obs.	Cal.(1)	Cal.(1)	Obs.−Cal.(1)	Obs.−Cal.(2)
800	8	1.03	1.30	1.08	−0.27	−0.05
	16	1.01	1.25	1.03	−0.24	−0.02
	24	0.97	1.22	1.00	−0.25	−0.03
900	24	0.63	0.63	0.61	0.00	+0.02
900	0.5	0.96	0.82	0.83	+0.14	+0.13
	1.0	.81	.76	.77	+0.05	+0.04
	2.0	.73	.70	.72	+0.03	+0.01
	4.0	.63	.65	.66	−0.02	−0.03
	8.0	.55	.60	.60	−0.05	−0.05
	16.0	.49	.54	.55	−0.05	−0.06
	32.0	.45	.49	.48	−0.04	−0.03
1000	0.5	0.65	0.60	0.62	+0.05	+0.03
	1.0	.56	.54	.56	+0.02	0.00
	2.0	.51	.49	.52	+0.02	−0.01
	4.0	.42	.43	.46	−0.01	−0.04
	8.0	.39	.39	.41	0.00	−0.02
	15.5	.37	.34	.36	+0.03	+0.01
	48.0	.29	.27	.29	+0.02	0.00
	141.5	.28	.21	.23	+0.07	+0.05
1100	0.5	0.39	0.38	0.38	0.01	+0.01
	1.0	.32	.33	.34	−0.01	−0.02
	2.0	.29	.29	.30	0.00	−0.01
	4.0	.28	.25	.25	+0.03	0.03
	16.0	.20	.18	.19	+0.02	+0.01
	40.8	.14	.14	.14	0.00	0.00
1110	24.0	0.10	0.15	0.15	−0.05	−0.05
1200	0.5	0.25	0.24	0.23	+0.01	+0.02
	1.0	.15	.21	.19	−0.06	−0.04
	2.25	.13	.17	.15	−0.04	−0.02
	4.0	.12	.14	.13	−0.02	−0.01
	8.0	.10	.12	.11	−0.02	−0.01
	16.0	.09	.09	.08	0.00	+0.01
	48.0	.06	.06	.06	0.00	0.00
1220	24.0	0.08	0.07	0.06	+0.01	+0.02
1400	0.5	0.09	0.10	0.06	−0.01	+0.03
1500	1.0	0.046	0.048	0.021	−0.002	+0.025

method permitted the use of small samples while maintaining the same degree of accuracy as was obtained by the usual combustion method for samples having much greater hydrogen contents.

Experimental Results

In order to determine the effect of the maximum temperature and the time of heating, a large sample of a specially selected anthracite coal was obtained and smaller samples of this heated at temperatures ranging from 800° to 1500° for periods of time ranging from 0.5 to 141.5 hours. The data so obtained are given in Table I. In the fourth and fifth columns are given values calculated on the basis of the following considerations. Anthracite coal is commonly supposed to have been formed by the thermal decomposition under pressure of organic matter. Preliminary examination of the data indicated that the hydrogen content was much more sensitive to a change in temperature than to a change in the length of time of heating at constant temperature, and that at constant temperature the decrease in hydrogen content with time was exponential. In addition to these facts, it was observed experimentally that no measurable thermal decomposition took place below some fairly high temperature, i.e., about 480° for this particular anthracite coal. To determine this initial temperature a sample of coal was placed in a quartz tube and connected to a Töpler pump. After a preliminary evacuation at room temperature, a furnace was raised into position surrounding the sample. The temperature was raised in 50° steps and maintained at each temperature until the rate of gas evolution was less than 0.1 c.c. per hour. The gas was collected and analyzed separately for each temperature interval. In Fig. 1 are plotted the total cubic centimeters of hydrogen evolved to the temperature indicated. The method of obtaining T_0 from these data is also illustrated.[1] The figures in brackets at each point represent the number of hours the sample was heated at each temperature.

Several equations were set up which qualitatively were in agreement with the facts outlined above.[2] Of these equations, one of the form

$$H = H_0 e^{-a(T-T_0)t^n} \qquad (1)$$

was chosen as most satisfactory. In this equation H represents the hydrogen content after heating at temperature T for time t for a material having an original hydrogen content H_0 and initial decomposition temperature T_0, a and n being empirical constants and e the base of natural logarithms. In calculating the values given in column 4 in Table I the value of T_0 was determined empirically from the data, while the value of H_0 was determined by analysis of the raw coal. The equation as used, replacing the constants by their numerical values, becomes

$$H = 2.10 \times 10^{-0.00210(T-720)t^{0.103}} \qquad (1a)$$

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[1] The method of measuring this temperature is essentially that of O. A. Nelson and G. A. Hulett: J. Ind. Eng. Chem., **12**, 40 (1920). Also see R. Holroyd and R. V. Wheeler: J. Chem. Soc., **1928**, 3197.

[2] I am indebted to Mr. G. G. Muller for developing these various equations.

Since the value of T_0 so obtained, i.e., 720°, did not agree with the experimental value of 480°, the following alternative form of equation was tried:

$$H = H_0 e^{-b(T-T_0)^c t^a} \tag{2}$$

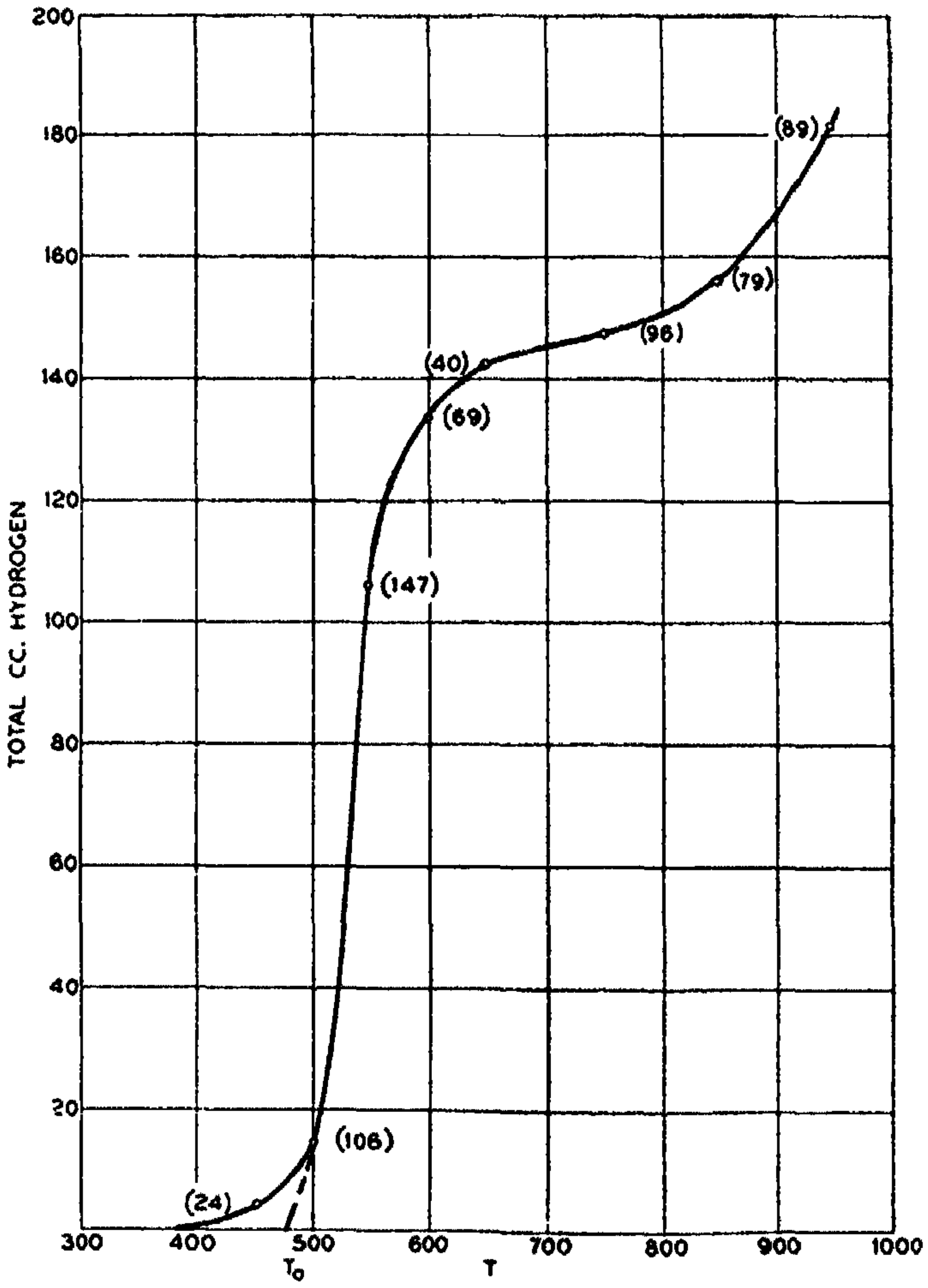

Fig. 1

Thermal Decomposition of Anthracite Coal #1, showing the total cubic centimeters of hydrogen evolved per gram of coal to and including the temperature indicated. The figures in brackets represent the number of hours the sample was maintained at each temperature.

where *b* and *c* are constants while the other symbols have the same significance as in equation (1), T_0 being the experimentally determined value. Replacing the constant with their numerical values, equation (2) becomes

$$H = 2.10 \times 10^{-0.00000477(T-480)^{1.92} t^{0.108}}. \tag{2a}$$

The values obtained by use of (2a) are given in column 5 of Table I. It is to be observed that either equation fits the data remarkably well considering the wide range of temperatures and times covered by the data. Equation (2a) appears slightly superior in that both the maximum positive and negative deviations obtained with it are less than those from equation (1a) and since it gives a much closer fit to the data at the lowest temperature used. Approximately half of the deviations are equal to or less than the probable error of the observed values, considering only analytical errors and not the errors due to possible variations in the method used for preparing the samples.

In order to test the equations further, a few samples were prepared from two other coals, one an anthracite coal having $H_o = 2.80\%$ and $T_o = 460°$, and the other, a coal sold as "Domestic Fuel," having $H_o = 4.03\%$ and $T_2 = 360°$. The observed and calculated values are given in Tables II and III respectively. The equations used for the calculations were,

for Anthracite #2

$$H = 2.80 \times 10^{-0.00238(T-700)t^{0.106}} \tag{1b}$$

$$H = 2.80 \times 10^{-0.0000222(T-460)^{1.05}t^{0.106}} \tag{2b}$$

and for "Domestic Fuel"

$$H = 4.03 \times 10^{-0.00170(T-410)t^{0.402}} \tag{1c}$$

$$H = 4.03 \times 10^{-0.000806(T-350)^{1.10}t^{0.402}} \tag{2c}$$

Again in the case of these two coals either equation appears to fit the data equally well. This might well be expected since both equations are three-constant equations, since in the first form T_o does not appear to have the significance assigned to it, and another constant "c" is necessary when the experimentally determined value is used. There is, however, a possibility

TABLE II

Calculated and Observed Values of Hydrogen Content of Anthracite #2

Temp. °C	Time in Hours	Hydrogen Content % Obs.	Cal.(1)	Cal. (2)	Obs.–Cal.(1)	Obs.–Cal.(2)
1000	0.5	0.57	0.61	0.60	–0.04	–0.03
	1.0	.54	.54	.54	0.00	0.00
	2.5	.45	.46	.46	–0.01	–0.01
	4.0	.42	.42	.41	0.00	+0.01
	8.0	.33	.36	.36	–0.03	–0.03
	16.0	.31	.31	.31	0.00	0.00
	24.0	.32	.28	.28	+0.04	+0.04
1200	0.5	0.22	0.22	0.21	0.00	+0.01
	1.0	.17	.18	.17	–0.01	0.00
	2.0	.18	.15	.14	+0.03	+0.04
	4.0	.13	.12	.11	+0.01	+0.02
	24.0	.10	.06	.06	+0.04	+0.04

that the value of T_0 determined from the hydrogen-content data does represent the minimum temperature at which hydrogen is liberated by "primary decomposition"[1] and that the lower temperature found experimentally is the result of a secondary decomposition of hydrocarbons liberated from the coal by heat.

TABLE III

Calculated and Observed Values of Hydrogen Content of "Domestic Fuel"

Temp. °C	Time in Hours	Hydrogen Content %				
		Obs.	Cal.(1)	Cal.(2)	Obs. – Cal.(1)	Obs. – Cal.(2)
1000	0.5	0.42	0.43	0.44	–0.01	–0.02
	1.0	.40	.40	.40	0.00	0.00
	2.0	.37	.37	.37	0.00	0.00
	4.0	.33	.34	.34	–0.01	–0.01
	8.0	.32	.31	.31	+0.01	+0.01
	16.0	.25	.28	.28	–0.03	–0.03
	32.0	.24	.25	.25	–0.01	–0.01
1200	0.5	0.22	0.20	0.20	0.02	+0.02
	1.0	.17	.18	.18	–0.01	–0.01
	2.0	.16	.16	.16	0.00	0.00
	4.0	.13	.14	.14	–0.01	–0.01
	8.0	.11	.13	.13	–0.02	–0.02
	24.0	.10	.10	.11	0.00	–0.01
	48.0	.11	.09	.09	0.02	+0.02

It is to be noted that the same value of the time exponent, 0.106, is obtained for both anthracite coals, while a much smaller value, 0.052, is obtained for the Domestic Fuel. This means that time is a less important factor in the case of the Domestic Fuel, the temperature being an even more predominant factor than in the case of the two other coals. It seems likely that this is to be somehow associated with the fact that the Domestic Fuel passes through a molten or plastic state, while both anthracite coals remain rigid solids throughout the temperature interval studied. This difference in the values of the time exponents for the anthracite coals and the Domestic Fuel is in accord with the hypothesis proposed in the earlier paper[2] to account for the presence of hydrogen chemically combined to carbon after exposure to high temperatures. It was suggested then (1) that the hydrogen was held by carbon atoms which were so situated with respect to neighboring atoms that they were unable to take their place in the normal graphite lattice and (2) that as the temperature was raised the mobility of the carbon atoms was increased and that a certain number would thereby be able to orient them-

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[1] See R. Holroyd and R. V. Wheeler: loc. cit.

[2] J. Am. Chem. Soc., 46, 824 (1924).

selves in a graphite lattice and in so doing transfer the force which previously had been sufficient to retain a hydrogen atom to the neighboring carbon atoms. During the molten stage, the carbon atoms of the Domestic Fuel are very mobile and the hydrogen is freely liberated, which is also reflected in the low hydrogen contents.

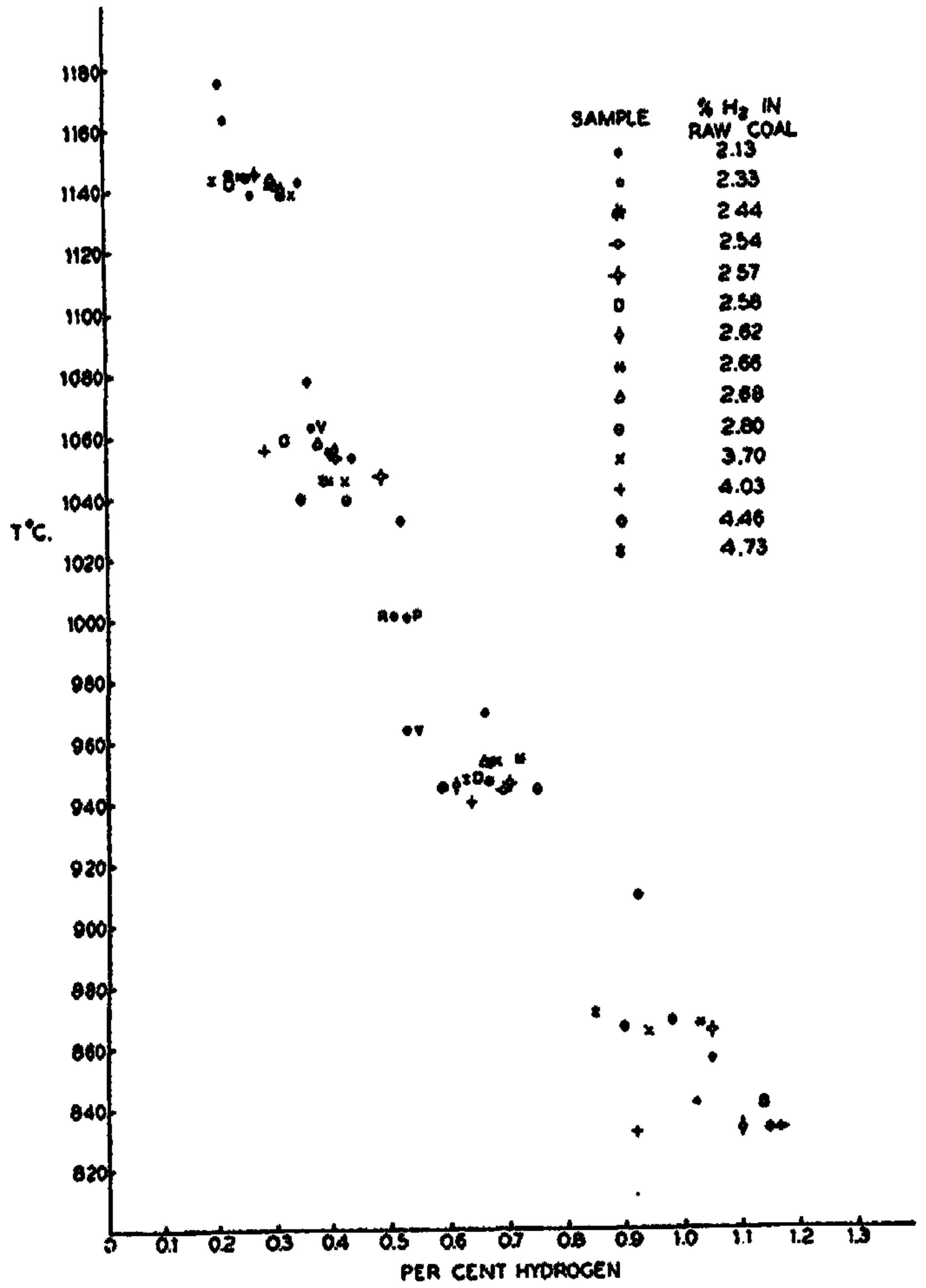

FIG. 2

A plot of hydrogen content data of fourteen different coals heated in an atmosphere of hydrogen for thirty minutes at the temperatures indicated. In addition there are included point "R," activated cocoanut charcoal; point "P," sugar charcoal, and two points "V," wood charcoals.

The few experiments conducted to determine the influence of previous heat treatment indicated that the treatments may be considered additive. For instance, a sample of Anthracite #1 was heated to 1200° for 4 hours reducing the hydrogen content to 0.12%. Subsequent heating at 800° for

4 hours left the hydrogen content unchanged. This would be expected from an examination of the equations. To reduce further this hydrogen content of 0.12% by an amount equal to the probable error of the determination would require, according to equation (2a), at least 800 years at 800°. Similarly, judging from the hydrogen content data alone, preheating at 800° is equivalent to a much shorter time at 1200° if the sample is later to be heated at 1200°.

In Fig. 2 are shown graphically the results obtained on 14 different samples of coal, all previously ground and sifted to 60-80 mesh and heated for 1/2 hour in an atmosphere of hydrogen at the temperature indicated. The hydrogen contents of the raw coals are given in the legend. All analyses are reported on an ash-free basis. It is evident from the figure that the hydrogen contents of the various samples fall within a comparatively small range for a given maximum temperature of treatment, the range becoming less at the higher temperatures. In general, the "softer" coals, i.e., those having the higher hydrogen contents in the raw state, yield products having less hydrogen than do the "harder" coals, which is in accord with the previous suggestion that in these cases the fusion of the coal allows the hydrogen to escape more readily than is the case with a non-fusible coal. Four points taken from the literature are also indicated on this figure. The point marked "R"[1] is for an activated cocoanut charcoal, that marked "P"[2] is for a sugar charcoal and the two marked "V"[3] are for wood charcoals. The fact that the hydrogen contents are so little dependent on the raw material suggests that the mechanism of thermal decomposition of carbonaceous materials at high temperatures is relatively simple and probably determined largely by the properties of the carbon atom itself. The mechanism proposed in a preceding paragraph considers a balance between the rigidity of the carbons and their energy contents.

In the preceding figure there was shown a point representing the hydrogen content of a charcoal activated in an oxidizing atmosphere at 1000°. This charcoal had the same hydrogen content as the other samples prepared in a hydrogen atmosphere. This would indicate that the hydrogen content was not of primary importance from the viewpoint of the activation process, but is determined solely by the temperature. Many experiments have been performed which fully substantiate this conclusion. In Table IV are given hydrogen analyses of samples prepared in different atmospheres. The only variable in the preparation was the gas passed over the carbon during the period of heating. The carbon was exposed in a thin layer to the gas in a rotating tube so that the granules would be uniformly affected by the atmosphere. With oxidizing atmospheres it was necessary to reset the temperature under the actual conditions of the test since the oxidation was sufficient to raise the temperature of a thermocouple in the furnace as much as 25°. The oxidizing gas was passed over the surface of the granules, the amount used

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[1] A. B. Ray: Chem. and Met. Eng., 28, 977 (1923).

[2] A. R. Powell: J. Am. Chem. Soc., 45, 1 (1923).

[3] Violette: Ann. Chim. Phys., 32, 322 (1853).

ranging from 80 to 800 c.c. (0.16 to 1.6 grams) per gram of sample. The charcoals changed regularly in appearance as the amount of oxidation increased, changing from solids with metallic luster to ones with the dull matte finish characteristic of adsorbent charcoals. It may be of interest to mention briefly at this time that the amount of carbon dioxide adsorbed at 0° and 760 mm pressure by these samples was increased by the oxidation from 8 c.c. per gram to 33 c.c. per gram for those prepared at 1000° and from 2 c.c. per gram to 24 c.c. per gram for those prepared at 1100°.

TABLE IV

The Hydrogen Content of Samples of Anthracite Coal No. 1 prepared at Different Temperatures in Hydrogen, Air, and Carbon Dioxide

Temp. °C	H_2	Air	CO_2	Cal.***
900	0.76 (4)*	0.67 (9)**	0.67 (6)**	0.78
1000	.49 (4)	.48 (5)	.47 (3)	.49
1050	.33 (1)	.36 (3)	.36 (3)	.37
1100	.29 (2)	.28 (3)	.28 (6)	.28
1150	.22 (7)	.22 (1)	.22 (8)	.21
1200	.20 (2)	.18 (3)	.17 (15)	.15
1250	.13 (1)	.13 (2)	.14 (1)	.11
1300	.10 (2)	.09 (1)	.09 (2)	.08

* The figures in the brackets are the number of samples prepared at the conditions indicated. The hydrogen content given is an average of this number.

** That these 900° values are too low, as may be judged from plotting the data, is to be attributed to the fact that they were prepared before it was appreciated that the use of an oxidizing gas raised the temperature of the furnace above that established with the furnace idle.

*** These samples were calculated using the following modified form of equation 2a:

$$H = 2.10 \times 10^{-0.00000527(T-450)^{1.47}}$$

assuming $t^{0.106}$ = constant = 1.105 which is combined with the constant "a" giving the value 5.27×10^{-6}.

Summary

Data have been given which show that at a constant high temperature, exceeding some temperature characteristic of the material, carbonaceous materials decrease in hydrogen content in a regular manner with increasing time of treatment. The temperatures ranged from 800° to 1500° and the times of heating ranged from 0.5 to 141.5 hours. Two equations of similar form are given, either of which reproduces the data within the experimental error for three different coals. It is pointed out that the effect of two separate heat treatments is additive. In all cases the hydrogen content was much more sensitive to a change in temperature than to a change in the length of time of heating at constant temperature.

From a study of the thermal decomposition of 14 different coals, ranging in hydrogen content from 2.13 to 4.73%, it was determined that the hydrogen contents, after heating for 0.5 hour at temperatures from about 900° to about

1200°, fell within a very narrow range. In general, the greater the hydrogen content of the raw coal the smaller the hydrogen content of the charcoal for a given treatment. This is particularly true where the coal passes through a plastic state. A hypothesis is presented to account for the phenomena observed.

It is shown that the atmosphere in which the sample is heated does not influence the hydrogen content of the resulting charcoal. Analyses of 93 samples prepared at temperatures ranging from 900 to 1300° in hydrogen, air and carbon dioxide are given to support this statement. These data indicate that the hydrogen content is not of primary importance from the viewpoint of the activation process as has previously been common belief.

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THE ACTION OF HYDROGEN SULPHIDE ON SOLUTIONS OF NITRIC ACID

BY H. B. DUNNICLIFF AND SARDAR MOHAMMAD

A Vogel[1] and N. A. F. Millon[2] found that hydrogen sulphide has no action nitric acid free from nitrogen peroxide while R. Kemper[3] ascribed the action with nitric acid (s.g., 1.18) at 25°C., giving sulphur, sulphuric acid, nitric oxide, nitrogen and ammonia, to traces of nitrogen peroxide produced by exposure of the nitric acid to air. I. W. F. Johnston[4] and C. Leconte[5] state that hydrogen sulphide reduces dilute nitric acid giving sulphur, sulphuric acid, ammonium sulphate and nitric oxide. P. T. Austin[6] observed that hydrogen sulphide burns in nitric acid vapour with a yellow flame giving clouds of nitrosulphuric acid. When hydrogen sulphide reacts with fuming nitric acid, J. Kessel[7] states that an explosion results while A. W. Hofmann[8] reports that the reaction takes place with incandescence. Frequent reference will be made to the recent work of Bancroft, Milligan and Gillette[9] on the reduction of nitric acid by metals and to the paper by L. S. Bagster[10] on "The Reaction between Nitrous Acid and Hydrogen Sulphide."

Part I. The Soluble Products of the Action of Hydrogen Sulphide on Nitric Acid Solution

In these experiments, hydrogen sulphide was prepared from ferrous sulphide and hydrochloric acid and purified by passing it first over dry iodine crystals and then through a dilute solution of sodium sulphide. The gas contains a little hydrogen, which was shown to have no action on solutions of nitric acid at ordinary temperatures. Before passing hydrogen sulphide, the air in the vessels was always displaced by carbon dioxide. It was observed that:—

1). Solutions containing less than 5% nitric acid are not attacked even if traces of nitrogen peroxide are added,

2). Solutions containing 5–30% nitric acid show no signs of reaction for some time but, if nitrogen peroxide is added, a violent reaction with rise of temperature follows, and

3) When a 40% solution is used the reaction takes place after an interval of apparent passivity called in this paper the "induction period."

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[1] J. Phys. **82**, 329 (1816).

[2] J. Pharm. Chem. (3) **2**, 179 (1741).

[3] Ann., **102**, 342 (1857).

[4] Edin. J. Sci., **6**, 65 (1832).

[5] Ann. Chim. Phys. (3) **21**, 180 (1847).

[6] Am. Chem. J., **11**, 172 (1889).

[7] Ber., **12**, 2305 (1879).

[8] Ber. **3**, 658 (1870).

[9] J. Phys. Chem., **28**, 492, 475, 754 (1924).

[10] J. Chem. Soc., **1928**, 2631.

This has also been noticed in the case of other reducing agents.[1] Ferrous sulphate, sodium sulphite, stannous chloride, and titanous chloride react with pure nitric acid after long standing. The induction period became longer when, before passing hydrogen sulphide, carbon dioxide was bubbled through the solution to remove any nitrogen peroxide resulting from the decomposition of nitric acid. Nitrogen peroxide is a well known catalyst in the action of nitric acid on metals, both in the presence and absence of sulphuric acid.[2] It also acts as a destabiliser to nitro-cellulose and nitroglycerine.

Milkiness due to sulphur appeared on the surface and spread rapidly through the liquid. When, after stopping the flow of hydrogen sulphide, the vessel was shaken, the atmosphere above the solution turned brown owing to the presence of nitrogen peroxide.

$$HNO_3 + H_2S = HNO_2 + H_2O + S \qquad (1)$$

$$HNO_3 + HNO_2 \rightleftharpoons H_2O + 2NO_2 \qquad (2)$$

The nitrous acid breaks down partly according to the reaction.[3]

$$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O \qquad (3)$$

$$\text{or } 2H^{\cdot} + 3(NO_2)' \rightleftharpoons 2NO + (NO_3)' + H_2O \qquad (3a)$$

Much work has been done on this reaction.[4] A. Klemenc and F. Pollack have shown that the decomposition depends on the removal of nitric oxide the presence of which hinders the reaction. A. V. Saposchnikoff observed that nitrous acid breaks up with water and nitrogen trioxide which can be extracted by organic solvents.

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad (4)$$

The nitrogen trioxide breaks down to nitric oxide and nitrogen peroxide

$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (5)$$

but equilibrium cannot be attained owing to the small solubility of nitric oxide and the hydration of the nitrogen peroxide. Nitrous acid decomposes spontaneously giving nitric oxide and the rate of decomposition is increased by the presence of nitric acid or by the passage of even inert gases through the solution. F. Raschig has shown that nitrous acid can oxidise nitrous oxide to nitric oxide and F. Hefti and W. Schilt find that hydrogen sulphide with it yields thiosulphuric acid accompanied by sulphur and ammonia.

Many have testified to the fact that, while the oxidising action of nitric acid usually ceases when it is reduced to nitric oxide, a normal reduction product of nitrous acid is nitrous oxide.[5]

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[1] Milligan and Gillette: J. Phys. Chem., 28, 754 (1924); Joss: 30, 1255 (1926).

[2] Gay-Lussac: Ann. Chim. Phys. (3), 6, 95 (1842); Russell: J. Chem. Soc., 27, 8 (1874).

[3] Montemartini: Atti Accad. Lincei, (4) 6II, 263 (1890).

[4] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 8, 459 et seq. (1928).

[5] Mellor: loc. cit., p. 463.

On passing a further supply of hydrogen sulphide, the brown colour disappeared as nitrogen peroxide reacts with hydrogen sulphide[1] giving sulphur, water and nitric oxide.

$$NO_2 + H_2S = H_2O + NO + S \qquad (6)$$

Nitric oxide reacts slowly with moist hydrogen sulphide giving some nitrous oxide and ammonium sulphide. When nitric oxide is bubbled through hydrogen sulphide solution, ammonia is formed (vide p. 1352).

In the first set of experiments with 40% nitric acid, four vessels B-E were connected in series with a reaction flask, A. The first, B, was empty and the others contained water, C, strong sulphuric acid, D, and acidified (H_2SO_4) ferrous sulphate, E, respectively. When the vessel, A, was shaken vigorously, the excess of hydrogen sulphide and the brown gas passed into the empty flask, B. Here a further deposit of sulphur was observed and the gas which passed on was colourless and contained hydrogen sulphide. The atmosphere over the liquid in A became colourless and ferrous sulphate acidified with sulphuric acid in E turned dark brown showing the presence of nitric oxide. The temperature in the flask, A, rose to about 70° C. and the solution turned bluish green. When hydrogen sulphide was passed into A surrounded by melting ice, the solution became dark green on standing. This, when exposed to the atmosphere or gently warmed, slowly became paler and emitted brownish red fumes of nitrogen peroxide from the decomposition of nitrous acid or nitrogen trioxide to which the green colour of such solutions is usually attributed.[2] When hydrogen sulphide was passed for a longer time, the liquid in A became paler with the deposition of sulphur. Finally, the whole of the sulphur coagulated and separated and the solution became clear.

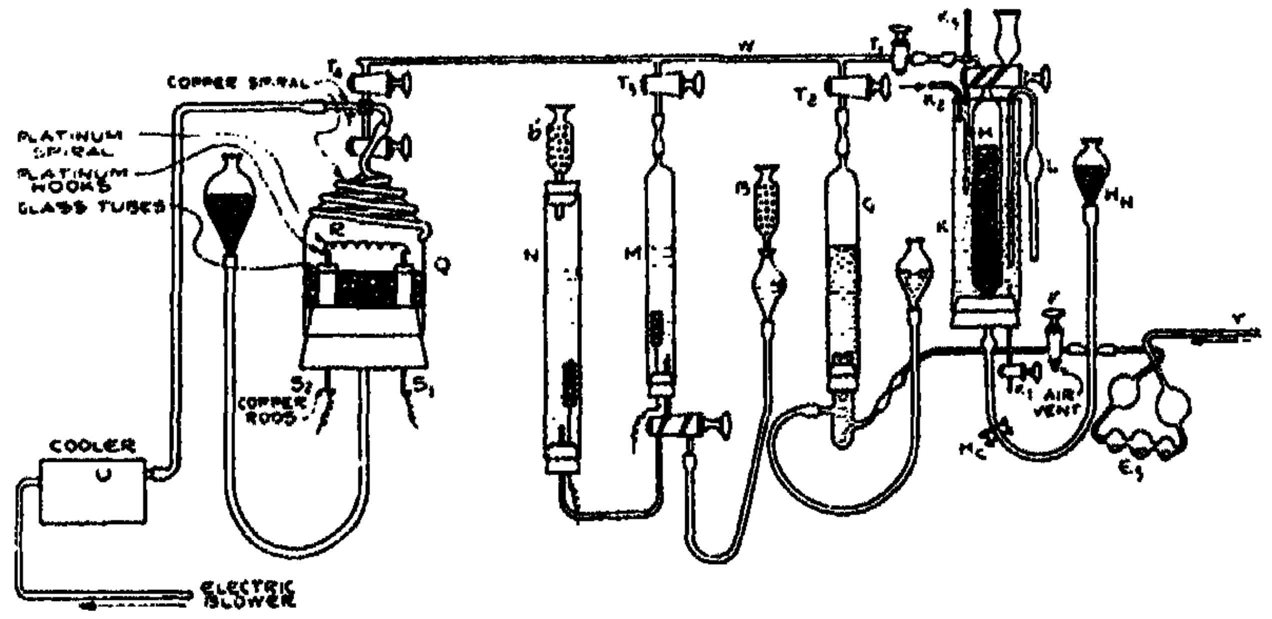

FIG. 1

At any time during the reaction, the solution in A gave tests for sulphuric acid, nitrous acid and "ammonium." Hydroxylamine which is known to be

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[1] Leconte: loc. cit.

[2] Lunge and Porschneff: Z. anorg. Chem., 1, 209 (1894); H. B. and M. Baker: J. Chem. Soc., 91, 1862 (1907); B. M. Jones: 105, 2310 (1914); Sanfourche: Ann. Chim. Phys., (10), 1, 5 (1924).

produced in the reduction of nitric acid by hydrogen sulphide under certain conditions was looked for repeatedly but was never detected. If it is an intermediate product

$$HNO_3 + 2S'' \longrightarrow NH_2OH + 2S(+ H_2O), \qquad (7)$$

it is decomposed as soon as formed, (vide equation (11)).

Feathery crystals, having the properties of nitrosylsulphonic acid or chamber crystals, $NO.O(HSO_3)$, appeared on the walls of the sulphuric acid flask, D.

Quantitative Determination of the Products of Reaction in Solution:

A constant stream of purified hydrogen sulphide gas was passed through 43% nitric acid for different intervals of time. The products formed in solution are ammonia and nitrous, nitric, and sulphuric acids. The solution was free from hydrogen sulphide. Sulphur was not determined in these experiments.

The methods, standardised by control experiments, were as follows:

"Ammonium." Sodium hydroxide solution was added in excess, steam blown through the solution and the ammonia collected in excess of standard sulphuric acid.

Nitrous acid by Lunge's potassium permanganate method.

Total nitrogen including dissolved nitrogen gases by Lunge's nitrometer method.

Sulphuric acid as barium sulphate.

Total acidity by titration against standard alkali.

Each set of results in Table I records a separate experiment. They show that:

1). The concentration of ammonia increases progressively but slowly and not in proportion to the nitric acid decomposed. If ammonia formed is not subsequently decomposed, its rate of formation is comparatively rapid at first and slower in the later stages of the reaction. In any case very little is found in the solution at any time.

2). The nitrous acid content shows a maximum at the period of greatest velocity of reaction (between 1.5 and 3 hours). The effect of the nitrogen is catalytic.

In his work on the reduction of nitric acid by metals, Veley[1] found that the start of the reaction is at first delayed and that the amount of nitrous acid increases to a maximum.

3). The total acidity decreases. The sulphuric acid formed has a marked influence on the rate of decomposition of the nitric acid and probably on the products formed: see also the results in Table II, p. 1349.

More detailed examination of Table I shows that

(a) up to 1½ hours, the nitric acid decomposed (11.97 grams) is very great compared with the sulphuric acid formed (4.471 grams). The equivalent

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[1] Phil. Trans., **182**A (1891).

TABLE I

Showing the nature and quantity of the reduction products in solution when hydrogen sulphide is passed through 42.93% nitric acid for different intervals of time

Composition of the solution; grm/100 c.c.

	Time in hours	$(NO_3)'$	$(NO_2)'$	NH_3	$(SO_4)''$
0.	0	42.25	—	—	—
1).	0.25	40.47	0.15	0.073	0.32
2).	0.75	39.00	0.41	0.115	2.21
3).	1.50	31.15	0.57	0.149	4.38
4).	3.00	8.90	0.21	1.110	20.13
5).	4.00	2.59	0.19	1.589	24.49
6).	5.25	1.97	0.15	1.730	27.88

	Time in hours	Total acidity as hydrogen	Colour of the solution of standing
0.	0	0.68	Colourless
1).	0.25	0.67	Pale Green
2).	0.75	0.66	Bluish Green
3).	1.50	0.61	Green
4).	3.00	0.49	Bluish Green
5).	4.00	0.46	Pale Green
6).	5.25	0.45	Colourless

quantity would be 9.31 grams. Reactions 1-3 above together with those given by Bagster[1].

$$3HNO_2 + S'' = 3HNO + SO_3 \ (+ \ 3H_2O) \qquad (8)$$

$$HNO_2 + S'' = HNO + S \ (+ \ H_2O) \qquad (9)$$

$$(HNO)_2 = H_2O + N_2O \qquad (10)$$

would account for (i) the large amount of nitric acid decomposed compared with the quantity of sulphuric acid formed, (ii) the evolution of nitrogen peroxide in certain circumstances and (iii) the formation of nitric and nitrous oxides. P. C. Rây and A. C. Ganguli[2] record the decomposition of hyponitrous acid giving nitrogen

$$5H_2N_2O_2 = 4H_2O \ 2HNO_3 + 4N_2 \qquad (11)$$

and A. Hantzsch and L. Kaufmann[3] that the same compound can yield ammonia

$$3H_2N_2O_2 = 2NH_3 + 2N_2O_3 \qquad (12)$$

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[1] Loc. cit.

[2] J. Chem. Soc., 91, 1399, 1866 (1897).

[3] Ann., 68, 299 (1899).

If hydroxylamine is an intermediate product (equation 7), it may be immediately decomposed giving nitrogen

$$H_2N_2O_2 + 2NH_2OH = 2N_2 + 4H_2O \qquad (13)$$

(b) From 1½ hours to 4 hours, the nitric acid decomposed is approximately equivalent to the sulphuric acid formed ($HNO_3 : H_2SO_4/2 = 461:419$). This suggests the reactions summarised in the equations:

$$S'' + 2HNO_3 = H_2SO_4 + 2NO \qquad (14)$$

$$6HNO_2 + 3S'' = 3H_2SO_4 + 3N_2 \qquad (15)$$

$$2HNO_3 + H_2S = \underset{\text{nitrosic acid}}{H_2N_2O_5} + S + H_2O \qquad (16)$$

$$= H_2SO_4 + N_2O + H_2O \qquad (17)$$

which with those given in (a) would account for the existence of nitrous oxide and much nitric oxide as well as nitrogen in the gaseous products at this stage (see Part III).

(c) When the concentration of nitric acid is very low, (under 3%), the sulphuric acid formed is in excess of that equivalent to the nitric acid decomposed. This is in agreement with the experiments described later in which it is shown that nitrogen is among the gaseous products and the inference is drawn that, since the power of oxidation of the nitric acid usually ceases when it is reduced to nitric oxide, oxidation by nitrous acid assisted by the increasing concentration of sulphuric acid is probably responsible for the nitrogen present (vide the reactions shown in paragraphs (a) and (b), p. 1347. Since solutions containing 5% nitric acid and less are not attacked by hydrogen sulphide (v.s.) it is clear that, at low concentrations, the nitric acid and its decomposition product, nitrous acid, have been rendered vulnerable to decomposition by the sulphuric acid present. This would suggest that HNO_3 and not $(NO_3)'$ ions are readily attacked. A. Kurtenacker[1] and Bagster[2] conclude that, in the reduction of nitrous acid, it is the nitrous acid (HNO_2) and not the nitrite ions, $(NO_2)'$, which are the active agent.

4). Hence the sulphuric acid developed has a very marked influence on the course of the reaction and the products formed. Others have drawn attention to this phenomenon e.g. Divers and Shimidzu,[3] from a study of the influence of sulphuric acid on the reduction of nitric acid by zinc, conclude that sulphuric acid has a specific hydrogenising effect upon nitric acid in the production of hydroxlamine but have not interpreted the mechanism of the reaction.

Part II. The Influence of Sulphuric Acid on the Reaction

A solution was made up containing 42.95 percent of nitric acid and 5% of sulphuric acid.

Through separate quantities of 100 c.cs. each of this mixture, hydrogen sulphide was passed continuously for different intervals of time. The con-

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[1] Monatsheft, 41, 91 (1920).

[2] Loc. cit.

[3] J. Chem. Soc., 47, 615 (1885).

ditions of experiment were comparable in that considerable excess of hydrogen sulphide was used. This fact is important in view of the results presented in Part III of the paper where it is shown, Table X, that gaseous products are evolved up to 6½ hours. This is the time required for "stasis" to be established when the hydrogen sulphide is admitted as required (vide p. 1356) and not passed in excess as in this set of experiments which are comparable with those detailed in Part I. The resulting solutions were analysed as described in Part I. Again hydroxylamine was not found.

The induction period was considerably increased but a trace of nitrogen peroxide started the reaction at once. Milligan and Gillette observed that, when much sulphuric acid is added to a mixture of nitric acid and ferrous sulphate, the period of induction is much increased and that traces of nitrous acid acted as a positive catalyser. E. J. Joss showed that, when a 17% solution of oxide-free nitric acid acts on copper, nitric oxide is evolved after 10 minutes. After the addition of 1% of sulphuric acid, nitric oxide was given after 20 minutes and, with 3% sulphuric acid, after 46 minutes. Higher concentrations decreased the time of inaction until, with 11% sulphuric acid,

TABLE II

Shows how the reduction products in solution vary when hydrogen sulphide is passed through a 42.95% solution of nitric acid containing 5% of Sulphuric acid

Strength of the nitric acid solution: 42.95 grm. per 100 c.c.
Sulphuric acid 4.898 gm. of $(SO_4)''$ per 100 c.c.

Composition of the solution gm/100 c.c.

	Time in hours	$(NO_3)'$	$(NO_2)'$	NH_3	Total	$(SO_4)''$ Formed in reaction
	0	42.27	—	—	4.90	—
i).	0.25	38.47	0.763	0.075	7.13	2.23
ii).	0.75	36.02	0.978	0.167	8.82	3.92
iii).	1.50	28.63	0.466	0.096	12.53	7.63
iv).	2.50	22.95	0.417	0.279	15.30	10.40
v).	3.50	23.25	0.275	0.259	15.15	10.25
vi).	5.00	23.34	0.422	0.175	14.93	10.03

	Time in hours	Total "acidity" in terms of hydrogen	Total "acidity" in terms of hydrogen, less "acidity" added (=0.10 grams).
	0	0.78	0.68
i).	0.25	0.75	0.65
ii).	0.75	0.73	0.63
iii).	1.50	0.67	0.57
iv).	2.50	0.64	0.54
v).	3.50	0.64	0.54
vi).	5.00	0.64	0.54

copper was attached more readily than with nitric acid alone. These results are explained on the basis of the increased solubility of nitric oxide by the presence of sulphuric acid.

The results of entirely separate experiments are recorded in Table II. The methods of experimentation and analysis were the same as those reported in Part I.

The results may be summarised as follows:—

1). The nitrous acid present is small in quantity and, after rising to a maximum value earlier than in the first, experiment, falls to a constant concentration which is higher than in the first set.

2). Since, in the first set of experiments, the ammonia is formed in quantity diminishing (assuming no decomposition) with increase in concentration of sulphuric acid, it is not surprising that, in these experiments, the amount of ammonia formed is less. Thus it appears that, if no ammonia is decomposed, the presence of sulphuric acid inhibits the formation of ammonia in the reduction of nitric acid by hydrogen sulphide. Hence the question as to whether ammonia is formed and subsequently decomposed by the nitrous acid giving nitrogen assumes importance.

3). When the concentration of nitric acid has fallen to 23% and the total sulphuric acid content is 15%, the reduction comes to a stand-still. This is a most unexpected result and its interpretation will be dealt with in detail below.

4). At no stage of the reaction is the amount of sulphuric acid formed equivalent to the nitric acid decomposed, the sulphuric acid formed being considerably less than that demanded. This would forecast a greater volume of gaseous products, i.e. oxides of nitrogen for a given rise in concentration of sulphuric acid. Experiments demonstrated that this is actually the case.

To review these observations in more detail:—

1). The higher concentration of nitrous acid may be due to the establishment of new stability relations involving the formation of small quantities of nitrosyl sulphonic acid

$$HNO_2 + H_2SO_4 \rightleftarrows NO.HSO_4 + H_2O \qquad (18)$$

which may be considered as nitrous acid stabilised by solution in sulphuric acid.[1] Dilution decomposes this acid with evolution of nitric oxide and formation of nitrous acid.

2). To ascertain whether ammonium salts are decomposed by the reaction, known amounts of ammonium sulphate or nitrate were added to the solution before passing hydrogen sulphide. The results are recorded in Table III. It was also shown that nitrogen is an important decomposition product (Table IX).

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[1] Milligan and Gillette: J. Phys. Chem., **28**, 744 (1924).

TABLE III

The decomposition of ammonium sulphate and ammonium nitrate in nitric acid by hydrogen sulphide:

Time for the passage of H_2S in hours	Ammonium salt used	Quantity of ammonium salt used in 100 c.c. in grm.	Ammonium contained in the salt in 100 c.c. gram.	Ammonium recovered after the reaction gram.	Ammonia lost gram.	% Loss
1.5	$(NH_4)_2SO_4$	2.86	0.74	0.37	0.36	48.7
3.0	$(NH_4)_2SO_4$	11.37	2.93	0.94	0.99	30.4
3.0	NH_4NO_3	4.71	1.00	0.27	0.74	74.0

Acworth[1] and Acworth and Armstrong[2] have shown that when ammonium nitrate is added to nitric acid used for the solution of copper, the principal gases evolved are nitrogen and nitrous oxide, and with zinc, mercury and iron, nitrogen is the principal gaseous product. E. J. Joss explains these results on the assumption that ammonium nitrite produced by the action of copper on nitric acid in the presence of ammonium nitrate decomposes under ordinary conditions into nitrogen and water.[3] Because ammonium nitrite can decompose into nitrogen and water, it is often assumed that the nitrogen produced in the reduction of nitric acid results from the interaction of nitrous acid and ammonium salts. Though this is possibly true in some cases, Bancroft shows that the generalisation is not justified because cases are known in which nitrogen is evolved when there is no reason to suppose that ammonia is formed at all. It was essential, therefore, to identify the gaseous products of the reaction with which this paper deals. This has been described in Part III and it is shown that nitrogen is not a product of the reduction of 40% nitric acid by hydrogen sulphide in the early stages. Hence the conclusion is drawn that the ammonia first formed is due to a side reaction and not to the main process of reduction of the nitric acid. There are three possibilities, all of which may be realised to some extent:

a). The ammonia is formed in solution by the reduction of nitrogen peroxide, nitrous acid or nitroxyl sulphuric acid

$$HNO_2 + 3S'' = NH_3 + 3S + (2H_2O) \qquad (19)$$

b). Hyponitrous acid can give ammonia (equation 12).

c). Ammonia may be produced by the action of hydrogen sulphide on nitric oxide.[1]

$$H_2S + NO \longrightarrow (NH_4)_2S + N_2O \qquad (20)$$

Scrubbed hydrogen sulphide was passed into water in a flask filled with scrubbed carbon dioxide gas to prevent the backward diffusion of oxygen (air). Nitric oxide was passed into the hydrogen sulphide solution and interaction

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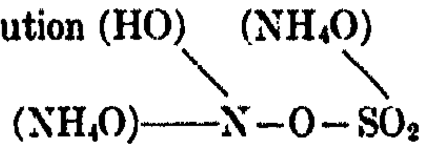
[1] J. Chem. Soc., **28**, 828 (1875).

[2] J. Chem. Soc., **32**, 67 (1877).

[3] Arndt: Z. physik. Chem., **39**, 64 (1901).

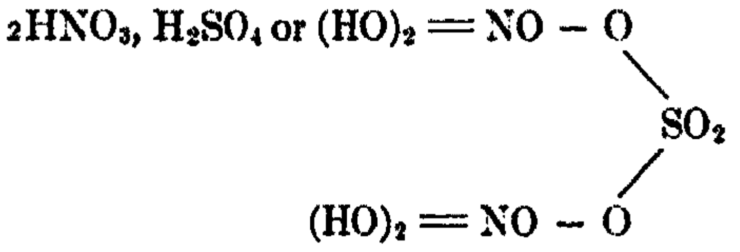
took place. Fumes of nitrogen peroxide were not observed inside the flask nor any reaction in the gas phase even when nitric oxide was in excess and the gases emitted from the flask gave brown fumes when they mixed with the air.[1] The solution contained much sulphur and, after removing hydrogen sulphide, it was found to give tests for ammonia readily. The liquid also contained sulphuric acid but nitric and nitrous acid were not detected even by the most delicate tests. This reaction is under further investigation. See also Bagster: loc. cit. Hydrogen sulphide interacts with nitrous acid giving much nitric oxide either in the presence of excess of nitric acid or of hydrogen sulphide[2] while nitric oxide with hydrogen sulphide and oxygen (Bagster, Table I) yields much ammonia and also nitrous oxide, nitrogen, and hydroxylamine. It is possible therefore that, in the later stages of the reaction under investigation, ammonia is formed by the action of hydrogen sulphide on nitric oxide and immediately decomposed giving nitrogen. As has been pointed out, however, it is not necessary to assume the intermediate formation of considerable quantities of ammonia and the authors are not of the opinion that this is the source of the nitrogen present.[3]

3). The remarkable condition of chemical "stasis" which comes about when the concentration of the nitric acid has fallen to 23% and that of the sulphuric acid has reached 15% may possibly be due to the combination of these two acids in solution at these specified percentages which correspond very roughly with equivalent quantities of the two acids, the nitric acid being slightly in excess. Salts of nitrato-sulphuric acid[4] HNO_3, H_2SO_4 or $(HO)_2 = NO.OSO_2.OH$ e.g. $KNO_3, KHSO_4$ or HNO_3, K_2SO_4 and NH_4NO_3, corresponding with the constitution



$$\begin{array}{l} \qquad\qquad (HO)\quad (NH_4O) \\ \qquad\qquad\quad \diagdown \qquad \diagdown \\ (NH_4O){-\!-}N{-}O{-}SO_2 \end{array}$$

have been obtained. It seems not improbable that a compound



$$2HNO_3, H_2SO_4 \text{ or } \begin{array}{l} (HO)_2 = NO - O \\ \qquad\qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad\qquad SO_2 \\ \qquad\qquad\qquad\quad \diagup \\ (HO)_2 = NO - O \end{array}$$

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[1] Leconte: loc. cit.; Lunge: Ber., 14, 2196 (1881).

[2] Bagster: loc. cit., 2683, Table II.

[3] Sardar Mohammad and H. D. Suri, working in this laboratory have shown that, when nitric oxide is bubbled through aqueous solutions of hydrogen sulphide in the absence of air, action takes place with the formation of ammonium compounds one of which is the tetrathionate. Hydroxylamine nitrate and nitrite are absent.

The gaseous products are nitrogen and nitrous oxide. Quantitative estimations show that nitrogen is the principal product comprising in the early stages 95% of the nitrogen—nitrous oxide mixture while, in the latter stages of the reaction, the proportion of nitrous oxide increases, the maximum recorded being 25% of the mixture.

When nitric oxide is bubbled through a solution of hydrogen sulphide in 5% sulphuric acid, only traces of ammonia are formed in the solution and the small quantity of gas formed is practically all nitrogen.

[4] Jacquelain: Ann. Chim. Phys., (2) 70, 310 (1839); Friedhein and Mozlin: Z. anorg. Chem., 6, 297 (1894).

corresponding with the above proportions of nitric and sulphuric acids may be formed in solution and that it may be passive to hydrogen sulphide. Physicochemical methods would determine whether this compound exists in solution or not. This investigation will be undertaken later.

In order to confirm these results, excess of hydrogen sulphide was bubbled through a solution containing 23% nitric acid and 15% sulphuric acid. No action resulted even after the passage of the gas for four hours at laboratory temperature (c.22°). If the action was started by the addition of traces of oxides of nitrogen, it subsided after a short time.

It should be noted that it would have been possible to pass through a stage in set I, Table I, in which the relative concentrations of the two acids were in equivalent proportions. This would have been in the 1.5–3 hours' period when it has been observed that the rate of decomposition was most rapid. By calculation this would have been when the nitric acid had fallen to about 19% and the sulphuric acid was about 14%. The fact that, in this set of experiments, the reaction did not cease is probably due to the lowness of the *total concentration* of the acids resulting in the dissociation of the postulated compound.

These are speculations and must be examined by scientific method but the possibility of their truth is contributed to by the fact that Friedheim and Mozlin obtained the salt $K_2SO_4.HNO_3$ referred to above from a solution containing one molecule of sulphuric acid and two molecules of nitric acid.

Part III. The Gaseous Products of the Reaction

The gases from the reaction flask were free from nitrogen peroxide and had to be examined for nitrous oxide, nitric oxide and nitrogen. Carbon dioxide and traces of hydrogen sulphide might be present. The former was removed by the potash in G (Fig. 1) and the latter by means of solid cupric phosphate.[1] See also Lunge's "Technical Gas Analysis," p. 249. Nitric oxide was estimated by absorbing it in a mixture of five volumes of saturated potassium bichromate solution with one volume of concentrated sulphuric acid.[2] The reagent is stable at ordinary temperatures and does not evolve oxygen when agitated with indifferent gases. Nitric oxide is quantitatively oxidised to nitric acid.

$$2NO = K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3H_2O + 2HNO_3 \quad (21)$$

Nitrogen and nitrous oxide were estimated in a specially designed apparatus (Fig. 1), which was a modified form of that used by Milligan for the same purpose. The cocks, T_1, T_2, T_3, and T_4 of a 5-way capillary tube, W, were connected with (1), a Lunge's nitrometer, H, (2), the tube, G, containing caustic potash solution and used later to receive the gases formed in actual experiments (3), a supply of pure hydrogen, M, prepared by the electrolysis of saturated baryta solution and (4), the combustion pipette, Q, respectively.

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[1] Harding and Johnson: J. Ind. Eng. Chem., 5, 836 (1913).

[2] Von Knorre: Chem. Ind., 25, 534 (1902).

The reservoir, B, and oxygen tube, N, were closed by guard tubes containing solid caustic potash. Any desired volume of hydrogen could be transferred into the Lunge's nitrometer. The nitrometer was cooled by means of a water jacket, K, containing supply, K_2, and outlet tubes, K_1, and a thermometer, K_3. The syringe bulb, L, was used to bubble air through the water to keep it stirred. The combustion pipette, Q, made from an inverted separating funnel, was surrounded by a copper spiral, T, perforated with small holes directed towards the pipette. Air, from an electric blower and chilled by passing through a spiral cooled by melting ice, was driven on to the glass walls and tap of the pipette to protect them from breakage during a combustion.

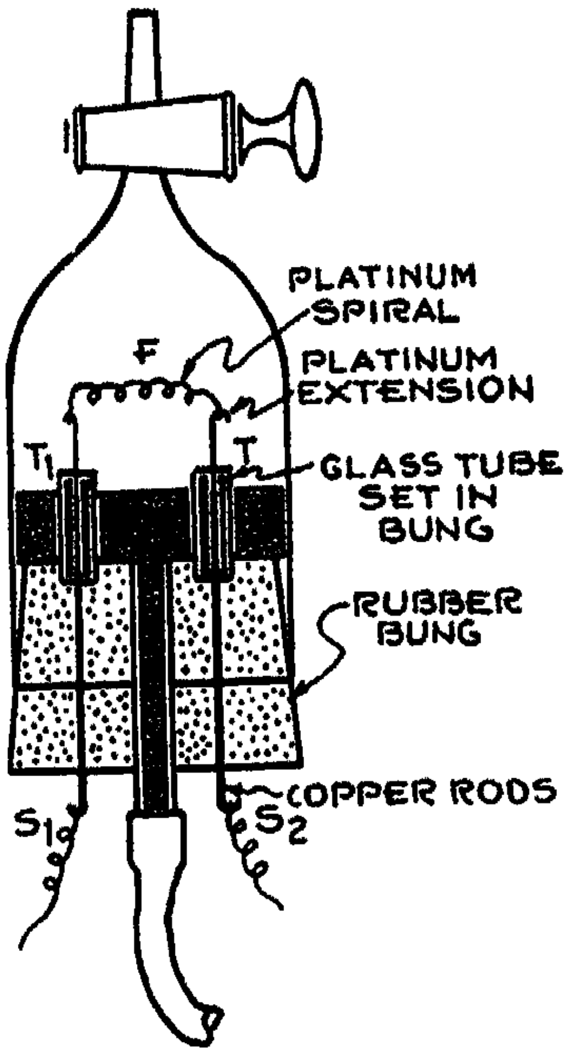

Fig. 2
Combustion Pipette

Through the rubber stopper of the pipette was passed a glass tube from the mercury reservoir and two copper rods, S_1 and S_2 (3.5 mm. diameter), having at their ends vertical sockets into which were set platinum rods (1 mm. diam.) ending in hooks between which the platinum heating spiral was stretched. Platinum extensions were used so that the copper rods were never exposed to the gases during combustion. The rods were connected through a switch and a rheostat to a battery. Fig. 2 makes these points clear. S_1 and S_2 are the copper rods, T_1 and T_2, the platinum rods and F, the platinum spiral. Mercury is shown as black and the apparatus is shown set for the heating of the spiral. The copper rods are covered and electrical connection between the two terminals is prevented by the setting in the rubber stopper, two glass tubes, T and T_1. It will be seen that the gases can be swept from the pipette and also that, when in the position shown, the spiral can be heated without fear of a short circuit. Before performing any experiment, air was completely expelled from the capillary tubes and pipette by filling them with mercury, using the nitrometer as a pump.

A measured volume of hydrogen was purified by drawing it several times into the combustion pipette (and heating the spiral) by raising and lowering the reservoir of the nitrometer. When the volume of the cooled gas was constant at atmospheric temperature and pressure, it was finally transferred to the combustion pipette. Pure nitrous oxide prepared by V. Meyer's method[1] and was then introduced into the nitrometer and measured. The

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[1] J. Chem. Soc., 141, 175 (1875).

screw clamp, H_0, on the pressure tubing was closed and the mercury reservoir of the nitrometer raised above the level of the three-way cock. The taps of the pipette and the nitrometer were opened and then the screw clamp just opened. The mercury in the nitrometer should rise so slowly as to be just perceptible. At the same time the spiral was made red hot and the cooling device started. In this way, the whole of the gas was slowly brought under combustion. The gases were then passed backwards and forwards slowly over the heated spiral until there was no further contraction when measured several times in the nitrometer by bringing the mercury reservoir to a fixed position. The gases were ultimately measured at atmospheric pressure and the contraction noted. This should be equal to the volume of nitrous oxide introduced. Actual values are given in Table IV showing a high degree of accuracy (about 0.3%).

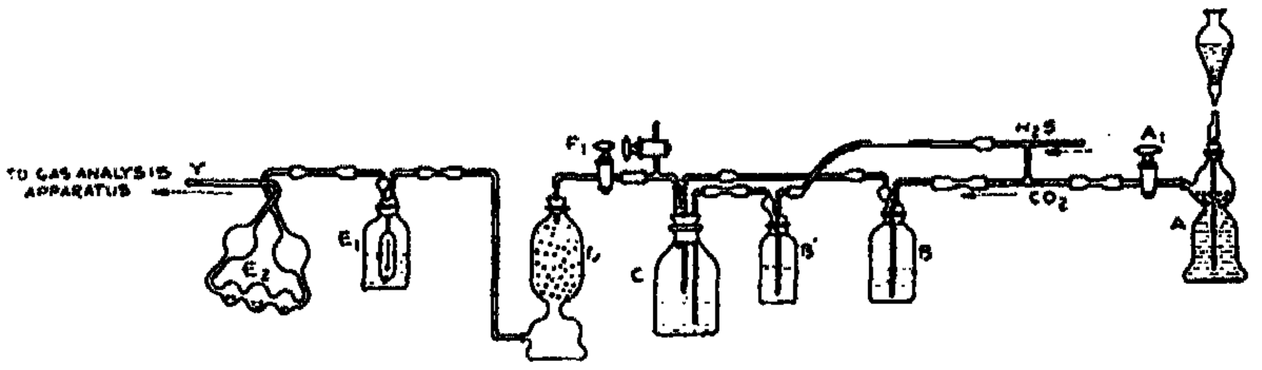

FIG. 3

TABLE IV

	Volume of hydrogen c.cs.	Volume of nitrous oxide c.cs.	Volume after combustion c.cs.	Contraction	Error %
i).	34.30	26.2	34.3	26.2	0
ii).	43.6	35.2	43.5	35.3	−0.3
iii).	40.2	30.	40.1	30.1	−0.3

Estimation of the Gaseous Products of the Reaction.

The apparatus is shown in Fig. 3. Two Kipps were used, one for making carbon dioxide by the action of hydrochloric acid on marble chips and the other for preparing hydrogen sulphide by treating blocks made of calcium sulphide and plaster of Paris with hydrochloric acid. The pressure necessary to force the carbon dioxide through the series of liquids was attained by making it possible to raise the acid reservoir of the Kipp to a considerable height by extending it with a long rubber tube. Carbon dioxide was scrubbed by sodium bicarbonate solution and hydrogen sulphide by dilute sodium sulphide. The tower, D, contained copper phosphate. The reaction flask, C, was connected by means of rubber tubing inside which paraffin wax had been run to prevent the oxides of nitrogen from attacking the rubber. The reaction flask could be shaken easily. To allow hydrogen sulphide to react on the nitric acid, the cock, F', was closed and the hydrogen sulphide cock opened, while the reaction flask was shaken. When the action ceased, the cock, F′, was opened and the products of reaction swept forward. In this way the correct amount of hydrogen sulphide for the reaction was admitted as required and its reaction completed before a further supply was taken in. Thus, excess of hydrogen sulphide was avoided. The absence of the free gas was shown by the fact that the cupric phosphate in the scrubber did not become brown or black. The absorbing vessels, E_1, E_2, E_3 contained potassium bichromate solution mixed with sulphuric acid. Cock F, (Fig. 1) could be connected either with the potassium hydroxide tube, G, or the air. The lower part of the tube, G, was connected by a rubber bung with the lower portion of the Schiff's nitrometer containing mercury. This arrangement prevented the liquid in G from being sucked back into the absorption vessels. Before commencing the experiment, air was driven out of the apparatus by a current of carbon dioxide. The scrubbing gas (CO_2) was let out through the cock, F, into the air. When, on trial, carbon dioxide was completely absorbed by the caustic potash in G, the experiment was commenced. It was observed that there was very little or no blackening of the cupric phosphate.

Unabsorbed gases were collected in G over caustic potash solution. When sufficient gas had collected, it was transferred to the nitrometer. After the experiment, the residual gases were driven into the vessel, G, by a current of carbon dioxide gas.

The residual gas was examined, as described above, for pure nitrous oxide and nitrogen. The standard bichromate solution was back titrated and the amount of nitric oxide absorbed was calculated. The results with the residual gas obtained by the passage of hydrogen sulphide up to 30 minutes showed that the gas is practically pure nitrous oxide (see footnote, p. 1358).

TABLE V

Combustion with the residual gas

	Volume of H_2	Volumes of the gas	Volume after the combustion	Contraction	Residual gas
i).	42.0	30.2	42.5	29.8	−0.5
ii).	40.0	29.3	40.7	29.6	+0.3
iii).	45.8	36.2	46.3	36.7	+0.5

The absence of nitrogen precludes the possibility of any reaction between ammonium salts and nitrous acid in the early stages. Some nitrogen would have been formed. Hence it is probable that, at first, ammonia is only formed as a result of side reactions and is not an important product of the main reaction.

In a carefully conducted experiment, all the soluble and gaseous products were determined. The results obtained after 40 minutes exposure to the gas as just described on p. 1356, (not bubbling unknown excess of the hydrogen sulphide) are shown in Table VI:

Table VI

Initial strength of nitric acid = 42.95%, HNO_3 containing 9.54 grams of nitrogen:

Analysis of products of reaction

HNO_3	= 39.82%	containing	8.85	grams	nitrogen.
HNO_3	= 0.46%	"	0.14	"	"
H_2SO_4	= 2.12%	"	—	—	
NH_3	= 0.16%	"	0.13	"	"
NO	= 0.81%	"	0.38	"	"
N_2O	= 0.21%	"	0.13	"	"
S	= 0.47%	"	—	—	
			9.63		

Error = +0.09 gram of nitrogen, equivalent to 0.4 gram of nitric acid.

The results of a second experiment (Table VIII) in which the solution was examined after 1 hour 20 minutes but from which the gases were only collected during the last hour of the experiment are also given.

Table VII

Initial strength of nitric acid = 42.95% HNO_3 containing 9.54 grams of nitrogen.

HNO_3 = 33.50% H_2SO_4 = 4.79%
HNO_2 = 0.18% NH_3 = 0.27%
NO = 1.24% containing 0.55 gram nitrogen.
N_2O = 0.28% " 0.18 gram nitrogen.
S = 0.81%

Again no nitrogen was found and the ratio of nitric oxide to nitrous oxide formed, in terms of nitrogen, remained the same, viz. 3:1.

In Table VIII are given the results of a further series of determinations in which the gaseous products were allowed to escape up to a certain time (col. i) and then the gaseous products collected between the times given in columns i and ii. Columns iii and iv show the proportions (per cent, by volume) in which nitrous oxide and nitrogen were found in the gaseous mixtures collected in the intervals between these times (cols. i & ii).

Table VIII

Collection of gases		Nitrous oxide	Nitrogen gas
Time started in hours	Time finished in hours	%	%
0	0.50	100.0	0.0
0.50	1.66	100.0	0.0
2.25	2.75	79.7	20.3
3.50	4.00	55.1	44.9
5.00	5.50	30.0	70.0

The amount of nitrous oxide decreases continuously.[1] Nitrogen makes its appearance and finally predominates though nitrous oxide is never completely absent. The appearance of nitrogen starts about the time when the rate of chemical action is a maximum and when the sulphuric acid formed is only a little less than equivalent to the amount of nitric acid decomposed. This is an interesting observation as it coincides with the fact that the more nearly the nitric (or nitrous) acid is exerting its maximum power of oxidation the greater the proportion of nitrogen in the gaseous products.

The increase in the concentration of sulphuric acid may be responsible in part for the instability of nitrous acid formed as an intermediate product or the explanation may be that the presence of sulphuric acid facilitates the formation of ammonia from nitric oxide by the action of hydrogen sulphide (vide Bagster: loc. cit). The ammonia would then be decomposed by the nitrous acid present and give nitrogen (vide supra p. 1356) though, as shown previously, it is not essential to suppose the formation of ammonia because nitrogen is one of the products of the reaction and one must not come too hastily to the conclusion that ammonia is the intermediate product. After a short exposure of the solution of nitric acid containing ammonium sulphate or nitrate to a current of hydrogen sulphide, much nitrogen was evolved together with nitric oxide. Table IX shows the analysis of the gas from two of these experiments.

TABLE IX

	Volume of hydrogen	Volume of the gas	Volume left after combustion	Contraction	N_2
i).	44.6	31.0	74.7	0.9	30.1
ii).	41.7	27.9	68.7	0.9	27.0

This suggests that nitrous acid is an early and important product of the reaction. Nitrous acid is almost certainly the procursor of hyponitrous acid, which, in acid solution, decomposes into water and nitrous oxide. This experiment also shows that nitrous acid—the parent of hyponitrous acid—is destroyed by ammonium salts. In this way, the side reaction prevents the appearance of the normal products of the reaction. These results also show that, in the early stages the action of hydrogen sulphide on nitric acid, ammonium salts are not formed and subsequently decomposed.

Hydrogen sulphide was passed into 43% nitric acid containing 5% of sulphuric acid as described on p. 1356. The reaction proceeds rapidly at first but slows down towards the finish. The gaseous products were collected between the intervals of time shown in Table X, columns ii and iii, and nitrous oxide and nitrogen were obtained in the proportions shown in columns iv and v.

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[1] A small amount of nitrous oxide is lost by absorption in the caustic potash solution G. This does not affect the general conclusions drawn.

Table X

Concentrations { Nitric acid = 42.95%
Sulphuric acid = 5.00%

No.	Time in hours		Nitrous oxide	Nitrogen	Ratio $\frac{N_2O}{N_2}$	Free HNO_3 still undecomposed
	Start	Finish	%	by volume		
1	0.05	0.10	Pure nitrous oxide never obtained.			
2	0.00	0.50	75.6	24.4	3 : 1	39.1%
3	0.50	1.50	The gas was practically all nitric oxide.			36.5%
4	1.75	2.25	58.5	41.5	3 : 2	—
5	2.75	3.00	38.8	61.2	2 : 3	29.1%
6	3.25	3.75	29.1	70.9	3 : 7	27.6%
7	5.00	5.50	23.0	77.0	2 : 7	24.1%
8	6.00	6.50	Negligible: only 4–5 c.cs. in all. A very little nitric oxide is evolved.			23.1%

Too much importance should not be attached to the time-composition relationship, cols. ii and iii and col. vii, as the method of working and the temperature variations make the relationship only of a general nature. When these results are compared with those in Table VIII, it will be seen (1) that the presence of sulphuric acid affects the action by eliminating a preliminary stage in which nitrous and nitric oxides are among the products of reaction but nitrogen is absent and (2) that, although pure nitrous oxide cannot be obtained, until chemical stasis sets in, a condition is never realised in which it is formed at all.

Part IV. Summary and Discussion

In order to facilitate the reading of the paper, much discussion has been introduced into the body of the report. To avoid duplication only the most general conclusions are summarised in this section.

1). Solutions containing 5% nitric acid and less are not attacked by hydrogen sulphide even if nitrous fumes are added.

2). Solutions of higher concentrations are attacked after a more or less long interval of time. This "induction" period is removed if nitrous fumes are introduced or slight decomposition of nitric acid is induced by insolation. The addition of sulphuric acid increases the induction period. A 43% (c.6.8N) solution of nitric acid was used.

3). The products of reaction are sulphuric acid, nitrous acid, ammonia, sulphur, nitric oxide, nitrous oxide and nitrogen.

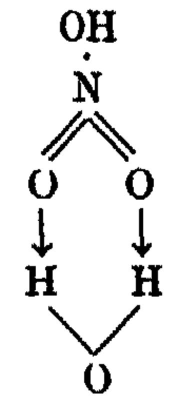
4). A possible explanation of the evolution of nitrogen in the later stages is that ammonia is formed and immediately decomposed. If this is so, ammonia is not formed in the early stages of the reaction in any quantity though there is evidence to show that it might be formed later. Apparently the presence of sulphuric acid exerts considerable influence on the formation of nitrogen. There are however explanations for the existence of nitrogen other than through the agency of ammonia as an intermediate compound, and it is probable that any ammonia formed is the result of side reactions or minor secondary reactions.

There is a concentration of ammonium salt below which there is no interaction with nitrous acid.

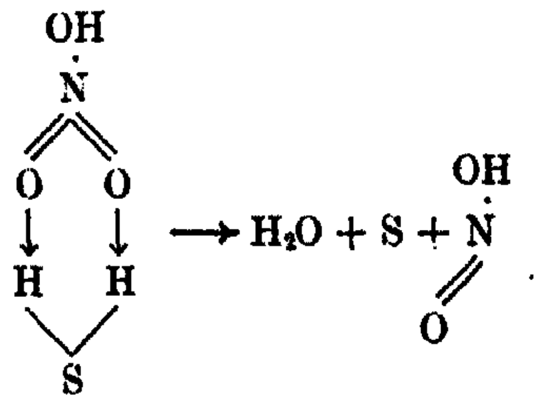
5). The presence of sulphuric acid affects the progress and ultimate products of the reaction. If to the nitric acid, sulphuric acid is added before passing hydrogen sulphide, the reaction stops when the concentration of the nitric acid has fallen to 23% and the total sulphuric acid concentration is 15%. These are roughly equivalent quantities but isotonic solutions of lower concentrations do not exhibit this stoppage in the progress of the reduction. It is probable that the nitric acid and sulphuric acid enter into a chemical combination which is inert to the action of hydrogen sulphide, but which at lower concentrations become decomposed or dissociated and attackable by hydrogen sulphide (p. 1352).

Suggestions regarding the mechanism of the formation of sulphuric acid are given on p. 1348.

6) From a study of absorption spectra and conductivity measurements A. Hantzsch[1] suggests that nitric acid consists of an equilibrium mixture of (i) O_2 NOH (pseudo-nitric acid), (ii) true acid present as hydroxonium salt $NO_3(H.OH_2)$ and (iii) acid forming salts like nitronium nitrate $(NO_3)_2$ $[(OH_3)]$ N. The hydroxonium salt may be



compared with the accepted views on sulphuric acid and leads one to the analogous but unstable hydrogen sulphide derivative which breaks down thus:



(22)

In strongly acid solutions this nitrous acid is probably the source of the nitric oxide and also of the nitrogen peroxide when it occurs. E. J. Joss[2]

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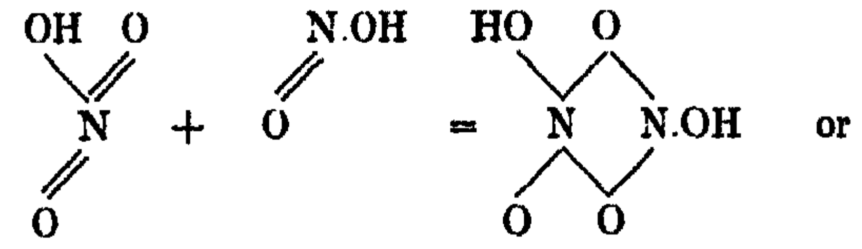
[1] Ber. 58, 941 (1925).

[2] J. Phys. Chem., 40, 1254 (1924).

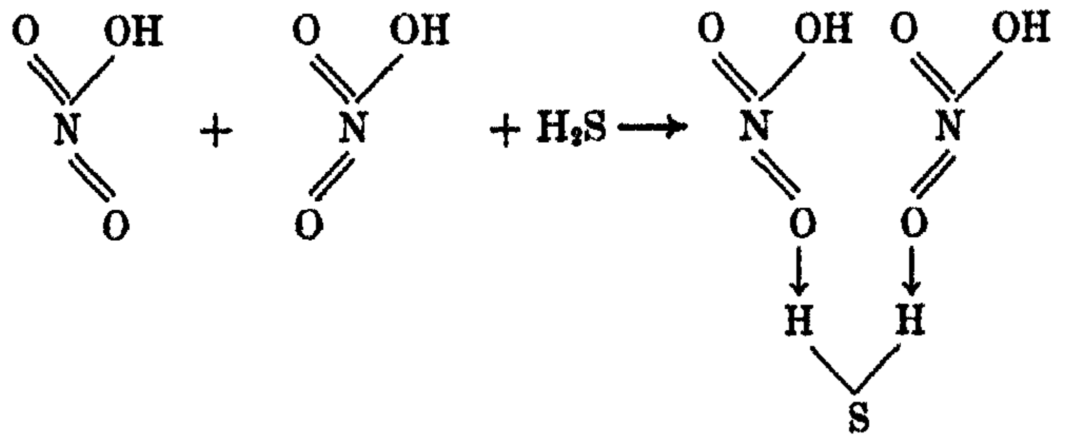
concluded that the depolariser in the reduction of nitric acid is nitrosic acid[1] ($H_2N_2O_5$); the formation of which in the action under review may take place in two ways:

1)

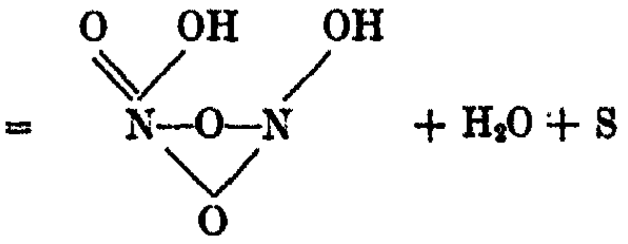


(23)

2)



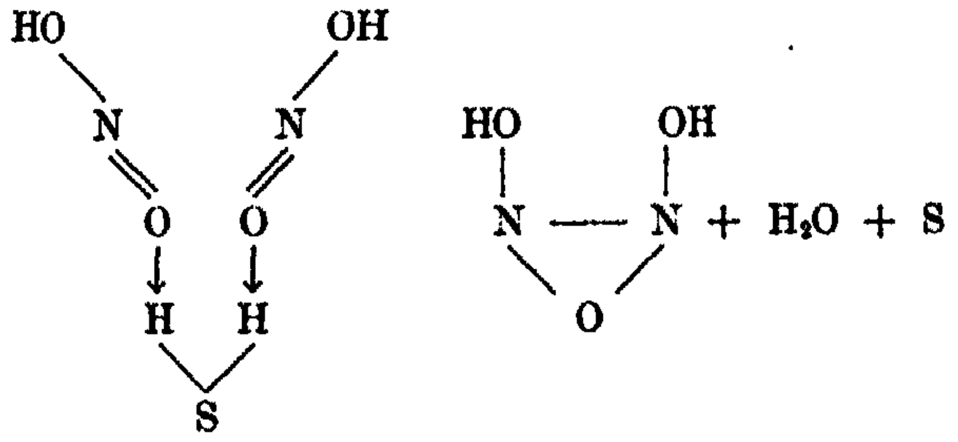
(24)



(25)

In other words nitric acid is activated owing to the formation of nitrosic acid, the nitrous acid being the catalyst. Nitrous acid also acts as an oxidising agent.

From nitrous acid, by the action of a reducing agent, Angeli's acid[2] or nitro-hydroxylamic acid is produced thus:



(26)

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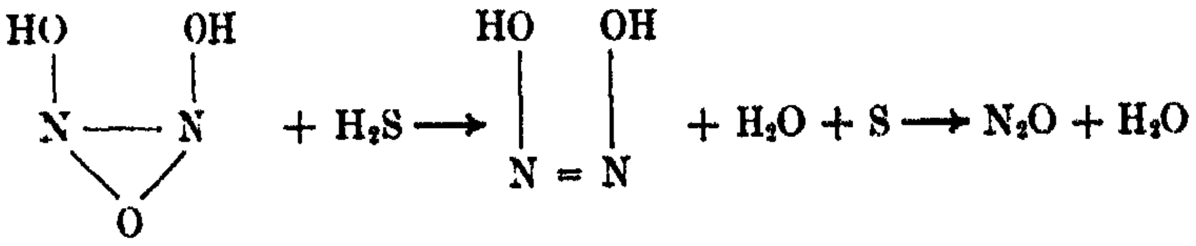
[1] Oddo: Gazz., 45 I, 413 (1915).

[2] Angeli: Gazz., 26 II, 245 (1897); Angelo and Angelico: 33 II, 245 (1903).

This is further reduced to $H_2N_2O_2$, hyponitrous acid, which, in acid solution, decomposes giving nitrous oxide and water



(27)

Hyponitrous acid can also decompose giving nitrogen (equation 13), or possibly ammonia (equation 12) one of the other potential sources of which is the action of hydrogen sulphide on nitric oxide (p. 1351).

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May 21, 1929.

THE REGIONAL ABSORPTION OF DYES BY GROWING CRYSTALS

BY ARTHUR G. MILLIGAN

Introduction

There are numerous references in physico-chemical literature to the coloration of crystals, grown from mother-liquors containing dye-stuffs in solution. As far back as 1854 de Senarmont showed that tinted crystals of strontium nitrate could be grown from a solution of the salt which had been coloured by extract of log-wood,[1] and many other examples have since been described. The phenomenon is not general: it occurs only with comparatively rare combinations of salt and dye, and it was quite by chance that one such combination attracted my attention in the course of an investigation of some of the factors influencing the crystallisation of salts from their aqueous solutions. I was attempting to retard and to control the growth of potash alum crystals by the addition of colloids to the mother-liquor when it was suggested to me by Dr. R. T. Beatty that interesting effects might be obtained with such semi-colloidal substances as the water-soluble aniline dyes. The effect with chlorazol sky-blue FF was arresting. Although it soon appeared that to investigate the phenomenon fully would demand more time and probably more specialised knowledge than I had at my command, I made a brief study of the salient features and established one or two facts which, I believe, constitute new knowledge on the subject. Dr. Beatty took a most helpful interest in the work and I owe him my thanks for many fruitful suggestions.

Apart from the bare fact that growing crystals will sometimes absorb a dye which has been dissolved in the mother-liquor and become more or less strongly coloured, it seems to be established that the phenomenon is comparatively rare, and cannot, at present, be predicted from a knowledge of the substances involved: When it does occur, the velocity of crystallisation is reduced, and R. Marc[2] affirms that growth entirely ceases before the concentration of dissolved salt has been lowered to the normal saturation value.

The most important facts emerging from the present investigation were, firstly, that the colour is confined to the wedge-shaped regions swept out by certain of the crystal faces as they grow, and, secondly, that the habit of a crystal may be profoundly modified by the absorption of a dye. The first of these facts seems to have narrowly escaped discovery by E. Perucca, who, in the course of a paper on optical activity in crystals[1] describes crystals of sodium chlorate artificially coloured by China blue extra dissolved in the mother-liquor. He noticed that the colour occurred only in patches, and his

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[1] Ann. Chim. Phys., 41, 319 (1854)

[2] Z. physik. Chem., 68, 104 (1909); 73, 685 (1910); 79, 71 (1912).

photographs leave no doubt that the absorption was regional in the sense of this paper; but he altogether failed to appreciate the true significance of his observations—that the coloured regions were the loci of particular faces during growth.

Experimental

Potash alum (K_2SO_4, $Al_2(SO_4)_3$. 24 H_2O) crystallises in the cubic system, and an aqueous solution, when cooled below its saturation temperature, deposits octahedral crystals, which can easily be grown to large dimensions. The octahedron {111} faces invariably predominate: other faces such as the cube {100} and rhombic dodecahedron {110} faces are usually small or absent.

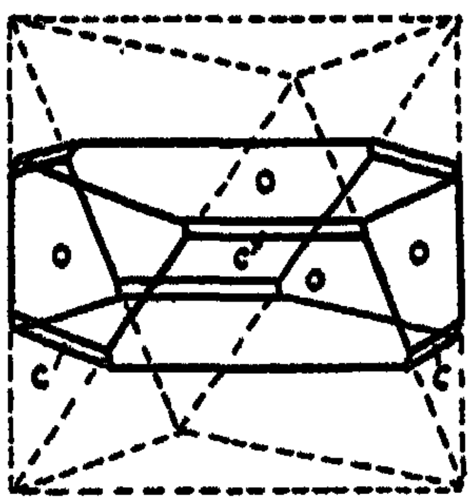

FIG. 1

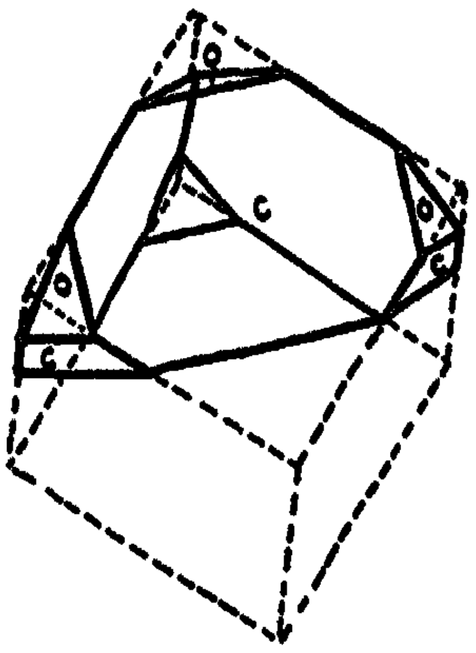

FIG. 2

When grown on the bottom of a crystallising dish, the octahedron are commonly somewhat flattened, as shown in Fig. 1, where a typical crystal, having large octahedron faces and small cube faces is shown in relation to the ideal octahedron, completed by dotted lines. This departure from the ideal has, of course, no crystallographic significance, and it will sometimes be convenient in the following pages to simplify discussion by considering only the ideal forms.

When a warm saturated solution of alum was strongly coloured by the addition of chlorazol sky-blue FF the crystals which separated on cooling were of a quite different habit. In them the cube faces predominated, the octahedron faces were reduced but still well developed, and rhombic dodecahedron faces occurred commonly. Fig. 2 shows such a crystal oriented like that in Fig. 1, to illustrate the change in habit due to the relative enlargement of the cube faces. The most remarkable and unexpected feature of these crystals, however, was the lozenge-shaped patch of intense blue colour which occupied the centre of each cube face although otherwise the crystals were colourless. In the first experiment, in which the concentration of dyestuff in

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[1] Nuovo Cimento, 18 II, 112 (1919).

the solution was very high, these patches were so dark as to be opaque and almost black. They were, moreover, sunk in shallow pits below the general level of the faces; and their surface had the granular appearance of Morocco leather. Fig. 3a is a sketch of a typical crystal. A very few small crystals had the form shown in Fig. 3b; they are essentially similar to the others, but have grown upon a base which is parallel to a cube and not to an octahedron face.

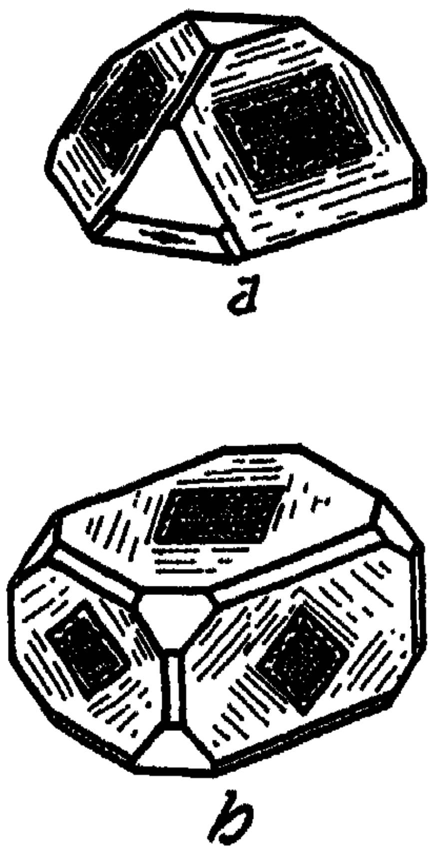

Fig. 3

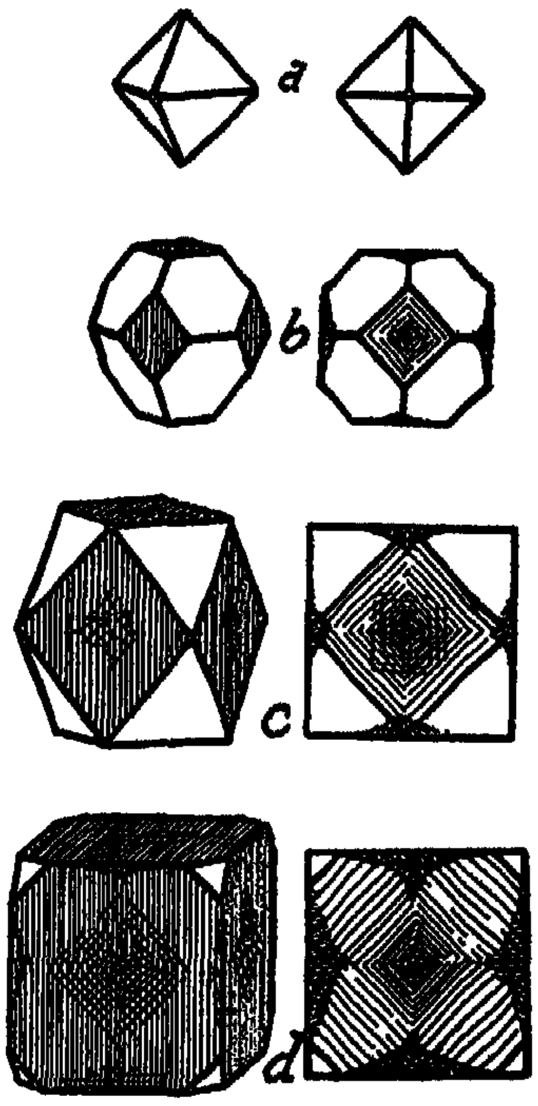

Fig. 4

A study of many crystals in different stages of growth helped to show how the peculiar disposition of colour arises. It is a commonplace paradox of crystallography that the fastest growing faces (those upon which the molecules of solute most readily and most rapidly deposit) tend *ipso facto* to disappear from the crystal habit: the persistent faces are those whose growth, outwards from the centre of the crystal, is slowest. This is obvious if we reflect that any face can extend laterally only by deposition of material upon the adjoining faces.

Alum crystals, under normal conditions, grow rapidly in directions perpendicular to the cube faces, which are consequently seldom developed. The predominant faces are those of the octahedron upon which the deposition of salt is relatively slow. Some of the smallest crystals found in the coloured solution were octahedral and colourless, and it seems probable that every crystal starts growth in this habit, for the great majority of dyed crystals, although essentially cubic, rested on a base parallel to an octahedron face (Fig. 2 and Fig. 3a), and the blue patches, which are associated with cube faces, were seen to be largely superficial. Sooner or later, however, tiny cube faces must form at the corners of the octahedron, as in Fig. 4a, which shows an ideal crystal both in perspective and in elevation. Immediately, for some reason not yet understood, these cube faces become coloured by association with dyestuff drawn from the solution. Further deposition upon them is inhibited by the presence of the colouring matter, and they begin to increase in area at the expense of the octahedron faces, upon which growth, unhampered by dye, is now relatively rapid (Figs. 4b and 4c).

In a moderate concentration of dye the octahedron faces are usually greatly reduced and may disappear completely (Fig. 4d). The resulting cubic crystals show very beautiful flower-like markings whose formation may be traced in Fig. 4. The clear portions of these crystals have been formed by deposition upon octahedron faces, once predominant but now vanished; the coloured regions by deposition upon ever enlarging cube faces. Every crystal thus bears in its own substance a legible record of its life-history, for on looking into the transparent design one can see what size each face has been at any stage of growth. For reasons already indicated only a very few tiny crystals closely approached the ideal shape shown in Fig. 4d: but the markings of larger and more distorted crystals are most readily understood by reference to the ideal diagram.

When the concentration of dyestuff is very high the phenomenon takes a slightly different course and produces crystals of the type first mentioned (Fig. 3) with octahedron faces still prominent and with the dye confined to intensely coloured, lozenge-shaped patches in shallow depressions in the middle of the cube faces. A study of many such crystals led me to accept the following explanation. Apparently the absorption of dye has in these cases so inhibited the growth upon cube faces as to stop it almost completely. The salt deposits upon octahedron faces only, and these, in consequence, are progressively reduced in area. A stage is reached when the area presented is inadequate for the reception of the crystallising salt, and, as the solution cools, the degree of supersaturation increases until at length an irregular kind of crystallisation occurs.[1] The octahedron faces, as it were, overflow their geometric limits, their further growth being accompanied by an irregular growth of the cube faces near their edges. As far as can be seen this new growth is built up, not by normal deposition on a cube face, which is prevented by the absorption of dye associated with it, but by the development of "vicinal" faces more or less inclined to the 100 plane, which seem to have but small affinity for the colouring matter. Such vicinal faces quite commonly occur in large alum crystals normally grown from a pure aqueous solution of the salt, and their appearance in these disturbing conditions is not sur-

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[1] One would expect that this increase in supersaturation might favour the formation of new crystal nuclei, and it was, in fact, observed that solutions containing large amounts of dyestuff tended always to produce numerous small crystals, rather than few large ones.

prising. Each cube face, then, shows a central lozenge of colour, surrounded by a raised ridge, poorly formed and not very clear, but apparently uncoloured except by occasional small inclusions of the blue solution. The sloping sides of the pit in which the coloured patch lies often seem to be formed by re-entrant octahedron faces; but here, too, the surface is very irregular.

This type of crystal is interesting as showing how strongly a dye may be concentrated on one "form" (in this instance the cube faces) without noticeably affecting any others which are present, and how completely growth may be prevented by absorption of the colour; but for further observation of the phenomenon the irregular growth was a very undesirable feature. In other experiments with alum and chlorazol sky-blue FF, therefore, a much smaller concentration of dyestuff was used, and in subsequent experiments with other dyes no absorption sufficiently intense to cause irregular growth was ever encountered.

A number of experiments were made with potash alum and water-soluble dyes other than chlorazol sky-blue FF. Many dyes (as, for example, the eosins) were largely or wholly salted out of solution by the concentration of alum necessary to give a solution saturated slightly above room temperature. Others, such as naphthol green, methylene blue, acid green G, etc., although they dissolved sufficiently to colour the solutions strongly, were not absorbed by the growing crystals. The best-formed crystals when removed from other-liquors containing these dyes were found to be clear and colourless; and any trace of colour in the poorer crystals was seen to be due to irregular inclusions of the coloured solution, and not to any true absorption of the dye in the substance of the crystal. Moreover these crystals were all octahedral in habit, with no more than a normal occurrence of small cube {100} and rhombic dodecahedron {110} faces.

Croceine scarlet 3B, which, like chlorazol sky-blue FF belongs to the azo-class of dyes, coloured the cube faces and favoured their development in a manner exactly analogous to that already described. The absorption, however, was not quite so strong and the inhibition of growth was less marked.

Methyl violet, a dye of the triphenylmethane type, was soluble only with difficulty in a saturated alum solution: but by boiling them together a solution was obtained which, after cooling and filtering, was fairly intensely coloured. On further cooling below the saturation temperature, this solution deposited numerous small crystals all of which were coloured a deep violet. The colour appeared to be uniformly distributed throughout the crystals, and they were all octahedral in habit. At first it seemed that in this instance the absorption of dye was not regional and had not modified the habit of growth. But closer inspection showed that cube faces were conspicuous by their rarity; only one small crystal showed a few tiny cubes at its corners and these faces were entirely free from dye, the clear, uncoloured wedges beneath them showing beautifully under a lens. The absorption of the dye was, in fact, strictly regional, but whereas, the other dyes had shown an affinity for the cube faces only, methyl violet avoided them and associated itself with the octahedron faces. The natural habit of alum being octahedral, the slowing down of growth upon these faces had no conspicuous effect, but the reduction of the already infrequent cube faces was an indication that the slowing down really does occur.

The results of experiments so far conducted on the growth of alum crystals from solutions coloured with various dyestuffs may be summarised as follows:

1. Dyestuffs may be classified according to their behaviour into the following classes.
    - A. Those precipitated by the high concentration of salt in the solution.
    - B. Those sufficiently soluble to colour the solution strongly, which may be subdivided into
        - a. Those which are not absorbed by the growing crystals.
        - b. Those which are absorbed, and either
            - α. Colour the cube faces, or
            - β. Colour the octahedron faces.
2. Soluble dyes which are not absorbed appear to exercise no influence on the growing crystals.
3. Dyes which are absorbed favour the development of the absorbing faces by retarding the deposition of salt upon them.
4. In every observed instance, absorption was regional, and not uniform.

It was of interest now to enquire whether other substances than alum would give similar results. Experiments were accordingly made with a few substances, chosen principally for the ease with which fair-sized crystals could be grown by simply cooling an aqueous solution below its saturation temperature.

The experiments with potassium chlorate, sodium chlorate, zinc sulphate and oxalic acid were not individually very satisfactory, because instances of absorption were rare, whereas inclusions of coloured solution were all too common and tended to mask the effect that was being studied. The most that I feel justified in saying of these experiments is that uniform absorption was never observed, and that regional absorption definitely occurred in the cases of sodium chlorate with phloxine, sodium chlorate with croccine scarlet 3B, and oxalic acid with rhodamine B. Excellent results, however, were obtained with sodium potassium tartrate ("Rochelle Salt," K $NaC_6H_4O_6$, $4H_2O$) of which large, clear crystals, free from irregularities and inclusions, can easily be grown by cooling an aqueous solution 5°-10° or more below the saturation temperature. The crystals are rhombic and the usual habit is a short prism showing principally the a {100}, b {010}, c {001}, m {110}, and r {210} faces, (Fig. 5) and in addition any or all of the faces n {120}, q {011}, O {111}, w $\{1\bar{1}1\}$ etc., which are usually inconspicuous and are not shown in the diagram. A crystal which grows upon the floor of the crystallising dish usually takes the form of one half of the ideal crystal, the base upon which it lies being a median plane of the ideal crystal and parallel to one of the principal faces, especially one of the three basal planes, a, b, and c. Fig. 6 gives sketches of two typical crystals: (a) is a short erect prism whose base is parallel to the c (001) face and which shows q {011} and w $\{1\bar{1}1\}$

faces in addition to those previously figured; (b) is a half prism lying on a base parallel to the b (1010) face, and the remainder of the ideal prism is indicated in dotted lines.

The azo dyes croceine scarlet 3B and chlorazol sky-blue FF, both of which had shown regional absorption upon the cube {100} faces of alum, gave excellent results with Rochelle salt also. Each was absorbed by the b {010} prism faces and gave brilliantly coloured wedges running from the centre of growth outwards to these faces. Fig. 7 is a sketch of a crystal coloured by chlorazol sky-blue FF. in which, for simplicity, the blue wedges are shown undistorted by refraction.

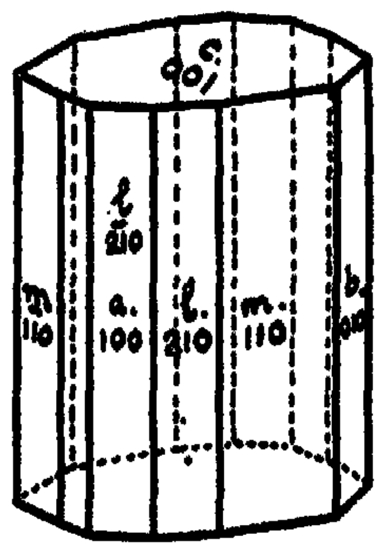

Fig. 5

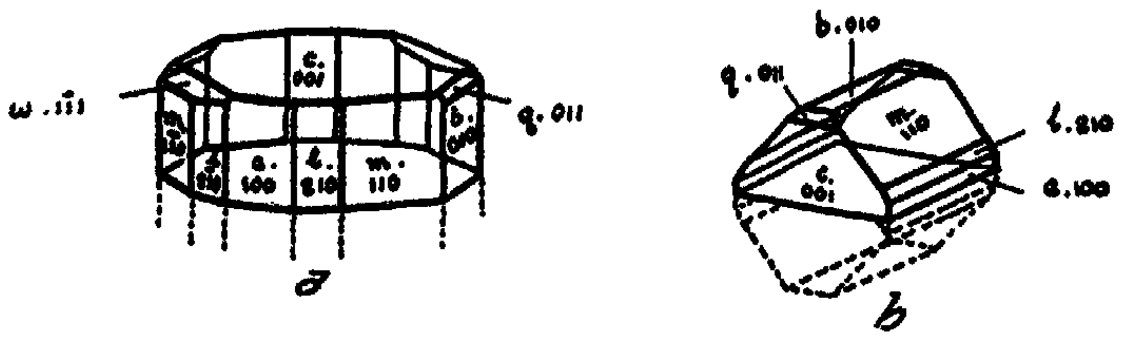

Fig. 6

Acid green G, a dye of the triphenylmethane class, which was not absorbed at all by alum crystals, gave with Rochelle salt an effect worthy of special mention. The dyestuff was largely precipitated by a saturation concentration of Rochelle salt, but, after boiling and filtering, sufficient remained in solution to impart a moderately good colour to the liquid. Crystals deposited from this solution showed regional absorption not only on the b {010} faces, but also, to a less extent, on the 1 {210} faces. Fig. 8 shows the appearance of the end of a typical prism examined by transmitted light. A strongly coloured wedge extended from the axis to each of the two b {010} faces, and four lighter wedges of approximately half the intensity ran from the axis to the four 1 {210} faces. Even in a prism 4.cm. long no trace of colour was perceptible in any of the regions swept out by the other faces. This was the only instance ever observed of a dye taking upon two *forms* simultaneously.

It is unfortunate that methyl violet, the only dye which was absorbed by the octahedron faces of alum, was very sparingly soluble in a saturated Rochelle Salt solution, and, in the greatest concentration which could be obtained, did not appear to colour the crystals at all.

Many dyes were tested with Rochelle Salt in a search for one which would colour some faces other than the b {010} faces, in order that the analogy with alum might be complete. The desired effect was at length obtained with phloxine, and less markedly with rose Bengal, both dyes of the eosin group. They were absorbed by the basal pinakoids, c {001} and by no other faces, so that a typical crystal had the appearance shown in Fig. 9, which should be compared with Fig. 7. It will be noticed that the distribution of colour indicates that the crystal grew at first in the form of a slender rod and that, at a certain stage, growth in the other two dimensions started abruptly.

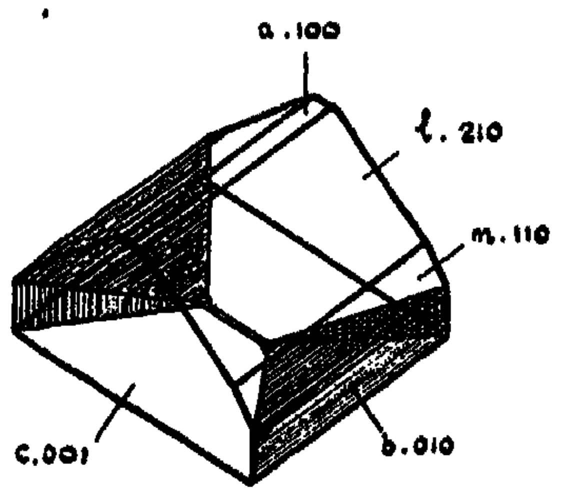

Fig. 7

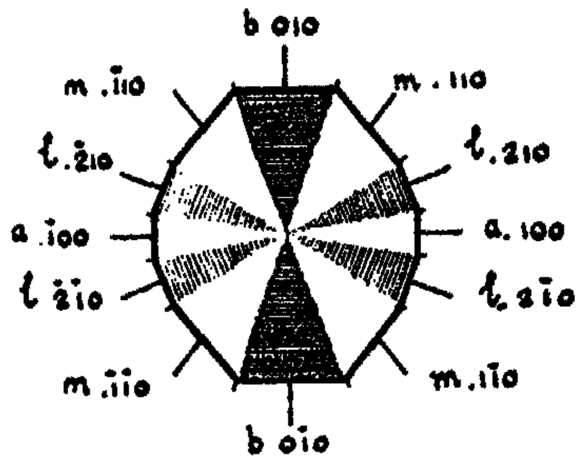

Fig. 8

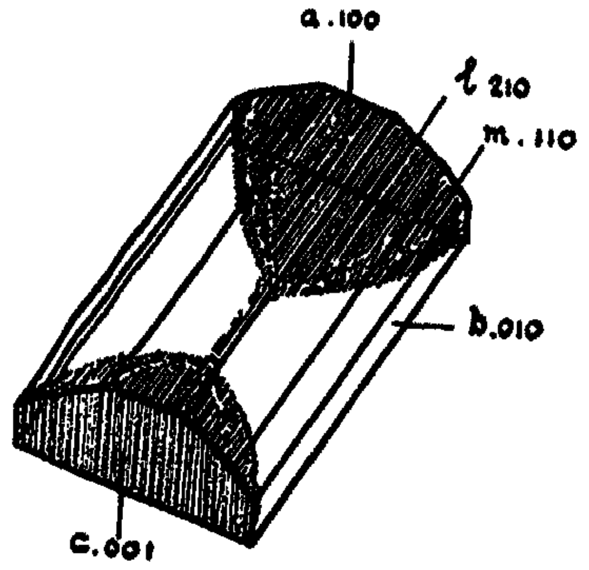

Fig. 9

This is not to be attributed to the presence of the dye, for the same thing is often indicated by the markings upon the base of a crystal normally grown from an uncoloured solution. Indeed, very little alteration in habit seemed to be caused in Rochelle Salt crystals by their absorption of dye: certainly nothing was ever observed comparable with the complete conversion of octahedral crystals into almost perfect cubes.

Eosin itself and other dyestuffs of this group either were insoluble in Rochelle Salt solution, or, being sparingly soluble, were not absorbed.

In view of the difference in behaviour of phloxine and rose Bengal with Rochelle Salt from that of chlorazol sky-blue FF and croceine scarlet 3B, it would have been interesting if alum crystals could have been grown in the presence of one of the former dyes, but unfortunately, they, as well as eosin, were almost entirely thrown out of solution by the salt.

Discussion

The essential features of the phenomenon which I have called regional absorption are clearly revealed in the experiments just described. It cannot be said with certainty that the absorption of dyes by growing crystals invariably takes this course but I think there is a strong probability that it does. I have found no evidence to the contrary; and if an example of a uniformly coloured crystal were known, it could be cited as an exception only if all the faces normally occurring in the uncoloured crystal were present in the coloured one.

While the effect is made clear, however, the cause remains obscure. I have not the opportunity to follow up the subject in greater detail, and I consider it to be the concern rather of colloid chemists and those interested in absorption and other surface phenomena. At present there is insufficient experimental evidence to build upon, and if I venture a hypothesis I do so tentatively and with due hesitation.

Marc[1] has already expressed the opinion that the slowing down of crystal growth by dyes is due to their adsorption on the crystal faces. The facts described in this paper undoubtedly support this view, since they show that the association of a dye is with the solid salt and not with the molecules still in solution, as might be the case if the colour absorption were uniform.

The factors causing adsorption on solid surfaces are many and varied, and are far from being clearly understood. In the case under consideration the deciding factor is one which varies from face to face of the same crystal. It may be the closeness of packing of the atoms on a particular plane: it may be the surface tension of the solvent, if one face should, for instance, be more thoroughly wetted than another.

In my opinion, however, the absorption of one dye by one *form* and of another dye by a different *form* of the same crystal, is most satisfactorily explained by supposing the deciding factor to be electrical. The oriented molecules in the crystal lattice must occasionally present upon certain planes a preponderance of polar atoms or groups of one sign. Such planes would attract to themselves ions, or, it may be, charged colloidal particles of the opposite sign. Most dyestuffs in solution are colloidal or semi-colloidal, and the faces on which they were adsorbed would on this assumption depend upon the sign of the charge they carry.

This hypothesis requires that chlorazol sky-blue FF and croceine scarlet 3B, on the other hand, should be oppositely charged from phloxine and methyl violet, on the other: since I suppose the {100} faces of alum and the {101} faces of Rochelle Salt to present a preponderance of polar group of one sign, while the {111} faces of alum and the {001} faces of Rochelle Salt have the opposite polarity.

I have been unable to obtain any useful information about the colloidal nature of these dyes: but *a priori* reasoning from their formulae (given below) leads one to expect that chlorazol sky-blue FF (I) and croceine scarlet 3B, (II) being sodium salts of sulphonic acids, would form, in solution, negatively charged ions or micelles; while methyl violet (III) the hydrochloride of an amino base would carry a positive charge. Phloxine (IV) however, is the potassium salt of a mixed phenolic-carboxylic acid heavily laden with halogen substituents, and there appears no reason why it should differ in behaviour from I and II.

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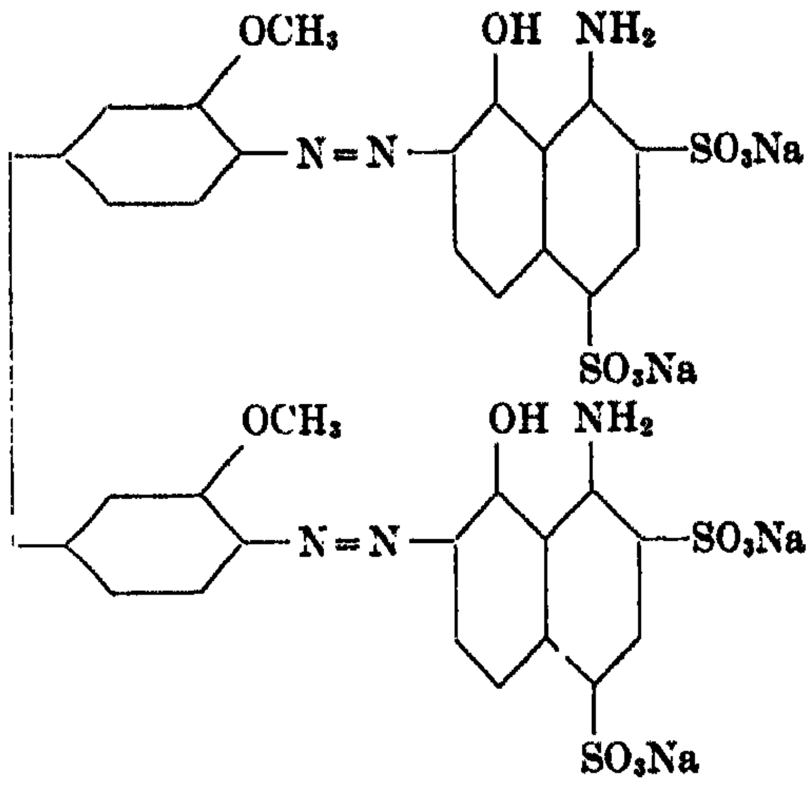
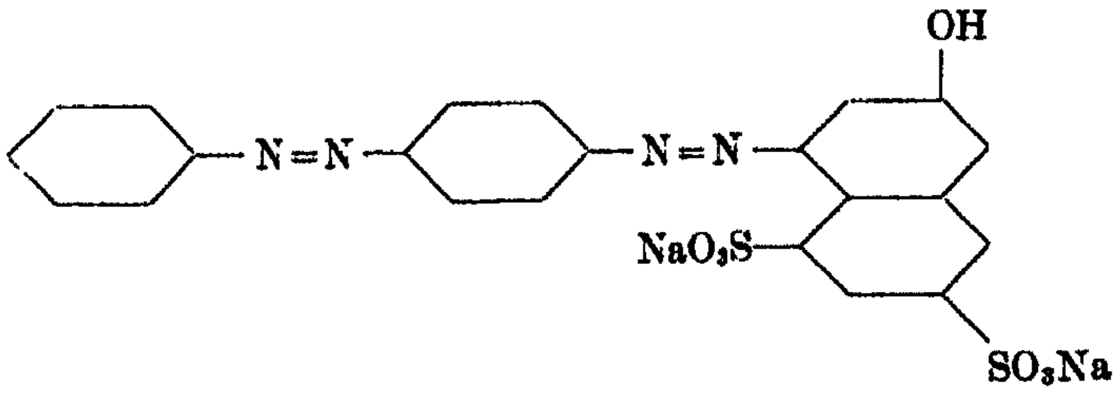
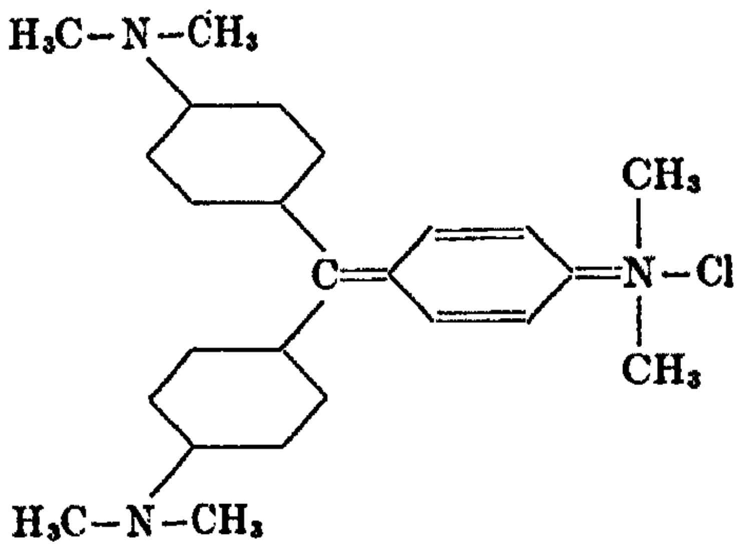
[1] Loc. cit.



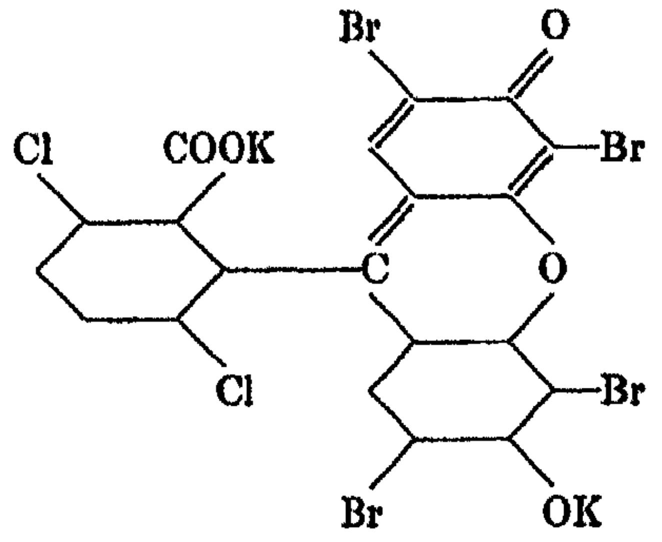
I



II



III



IV

It is particularly unfortunate that the two dyes which were found to be absorbed by both potash alum and Rochelle salt fall in the same category. An instance of a dye colouring the {111} faces of alum and the {001} faces of Rochelle Salt would have strengthened the hypothesis now suggested: a single contrary instance would have disproved it. As it is, the phenomenon perhaps merits the attention of the colloid chemist; and, if eventually the hypothesis I put forward should prove substantially correct it is probable that the regional absorption (should we say the regional *adsorption?*) of dyes by growing crystals might have valuable applications in the elucidation of crystal structures.

My thanks are due to Dr. R. T. Beatty of the Admiralty Research Laboratory, Teddington, for his keen interest and valuable suggestions, and to the Director of Scientific Research to the Admiralty for permission to publish this paper.

April 16, 1929.

MEMBRANE POTENTIALS[*]

BY JOHN M. ORT AND W. G. FRANCE

Introduction

In the use of thermodynamic equations to account for experimentally determined potentials of cells employing membranes, the membranes are assumed to be ideal. That is, it is assumed that there is no potential difference across the membrane other than that due to the effect upon which the equation is based. Des Coudres,[1] Donnan, Prideaux, Loeb, and others have gathered much experimental data in support of such equations. The agreement between theoretical and experimental results has not always been within the limits of experimental error. For example, Donnan and Allmand say, —"the phenomena are not so simple as supposed in the theory mentioned." However, the approximation of the observed values to the calculated values often has been too close, to doubt that the theory underlying these calculations is sound.

Many have observed that different membranes carry different electrical charges under a given set of conditions.[2] And it has been further observed that the charge for a given material changes under different conditions and can even be reversed in sign in suitable surroundings.

It has also been pointed out that some of the discrepancies between the theoretical values and the values obtained by membrane potential measurements may be due to these charges, which are specific for each membrane under the conditions employed.

Apparently there are no published data in which the specific charges of the membranes are considered in the accurate determination of membrane potentials. In this investigation, these charges have been considered in the measurement of one type of cell in which a membrane potential exists. These data indicate that there are two potential effects involved, one, the specific potential due to the nature of the membrane and electrolyte, and the other a mathematically calculable potential.

The particular cell chosen for study was first described by Des Coudres. It is produced by the pressure of a column of mercury resting on a membrane impermeable to liquid mercury, but permeable to Hg^+ ions, to the water, and to the other ions of the electrolyte in contact with the opposite side of the membrane. By this pressure, Hg^+ ions are forced through the membrane,

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[*] From the thesis presented to the Graduate School of the Ohio State University for the degree of Doctor of Philosophy, June 1924, by John M. Ort.

[1] Des Coudres: Wied. Ann., **46**, 292 (1892); Donnan and Harris: J. Chem Soc., **99**, 1554 (1911); Donnan and Garner: **115**, 1313 (1919); Donnan and Green: Proc. Roy. Soc., (A) **90**, 450 (1914); Donnan and Allmand: J. Chem. Soc., **105**, 1963 (1914); Prideaux: Trans. Faraday Soc., **10**, 160 (1914); Loeb: "Proteins and the Theory of Colloidal Behavior," Chapter VIII.

[2] Perrin: J. Chim. phys., **2**, 601 (1904); **3**, 50 (1905); Bartell and Hocker: J. Am. Chem. Soc., **38**, 1029 (1916); Coehn and Franken: Ann. Physik, (4) **48**, 1005 (1915).

tending to leave the liquid mercury charged negatively. Because of electrostatic attraction, equilibrium in this passage of Hg^+ ions through the membrane is reached when the work which would be necessary to force a gram equivalent of Hg^+ ions away from the negatively-charged liquid mercury is just equal to the work which would be necessary to raise the weight of the gram equivalent of ions through a distance equal to the height of the mercury column above the membrane. Hence, the potential difference of this cell as measured across an ideal membrane, should, as Des Coudres derived it, be given by the equation:

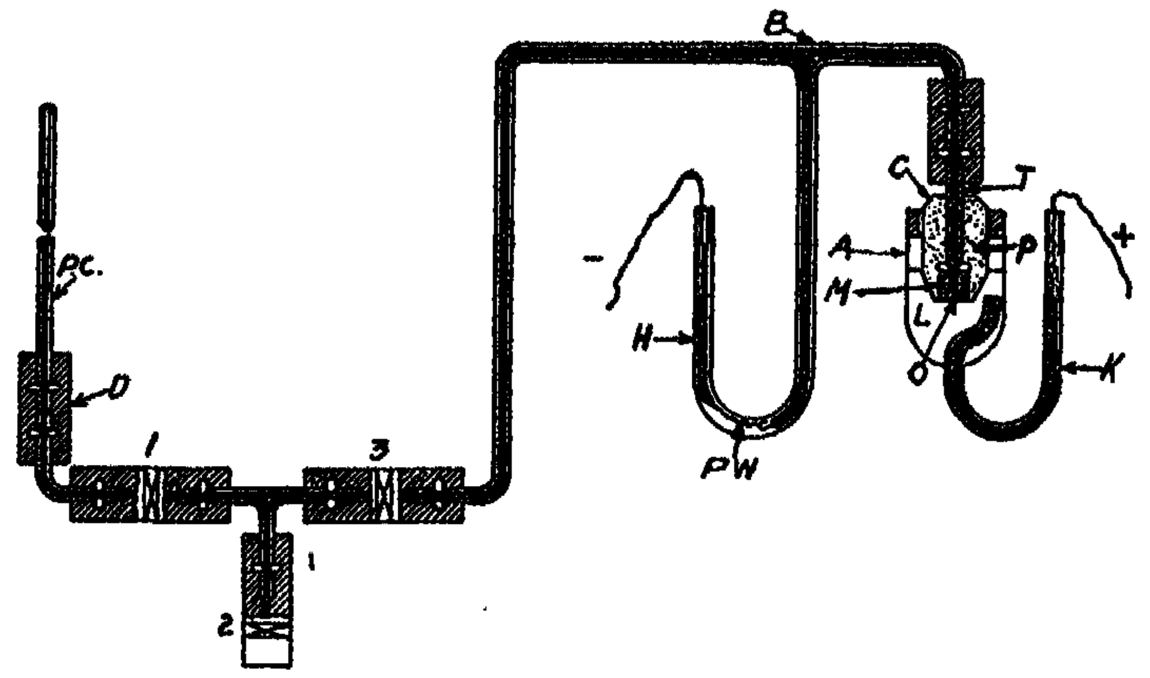

FIG. 1

$$E = \frac{Q \times 10^{-1} \text{ volts}}{S},$$

in which E = the potential per each atmosphere of pressure of the liquid mercury column, Q = the electrochemical equivalent of the Hg^+ ion, and S = the density of the liquid mercury in the pressure column. This amounts to very nearly 1 microvolt per height of 5 cms.

Des Coudres used parchment paper membranes. While some experiments were made with parchment paper, and also with gold-beaters' skin, the data given here were gathered only from collodion membranes. Des Coudres obtained results which checked his equation only approximately. His discrepancies ranged from 3% to 20%, growing larger at the higher pressures and potentials, and were probably due somewhat to polarization. The highest pressure he used was 113 cms. of mercury. He attributed these differences to errors in his potential measurements. Our data also show that the measured cell potentials are not always in agreement with those calculated. Indeed, they are often many times the calculated values, and sometimes opposite in sign. However, after the specific charge of the membrane becomes constant, then the measured additional potentials, which are due to the pressure effect, agree with the calculated increases within the limits of error of the measurements.

Apparatus

The modified form of the Des Coudres cell used is shown in Fig. 1. All glass parts were of Pyrex except the pressure column, P. C., which was made of ordinary soft-glass tubing of about 5 mm. bore. The membrane M was folded over the bottom end of the tube T and pressed against the hole O (about 5 mm. in diameter) in the bottom of the larger tube C. Paraffin in the space P, held these parts rigidly in place. Thus the membrane was in contact with mercury on the top side and with the electrolyte L, on its bottom side. The heavy, wire-wound, rubber pressure tube connections are shown in cross section. Electrical connection to the mercury under pressure was made through the sealed in platinum wire, P. W. The potentials, as recorded below, were read between the mercury in the tubes at H and K with a White Double Potentiometer. The vessel A and tube H were immersed in an oil thermostat which held the temperature constant to within a hundredth of a degree Centigrade.

The Pressure Effect

After standing for over two weeks to allow the specific charge to become fairly constant, the effect of mercury pressure on the membrane could be studied. Table I shows the result of a typical pressure run.

Table I

I Time in Minutes	II Pressure in cms. Hg.	III Observed cell potential Microvolts	IV Change from Observed Microvolts	V Last Reading Calculated Microvolts
0	125	−34	0	0
120	125	−36	− 2	0
165	125	−41	− 5	0
195	125	−37	+ 4	0
203	155	−43	− 6	− 6
209	155	−43	0	0
211	115	−35	+ 8	+ 8
217	115	−35	0	0
218	75	−27	+ 8	+ 8
263	75	−30	− 3	0
265	40	−23	+ 7	+ 7
271	40	−23	0	0
272	0	−15	+ 8	+ 8
278	0	−15	0	0
280	40	−23	− 8	− 8
287	40	−22	+ 1	0
289	75	−29	− 7	− 7
293	75	−29	0	0
296	150	−45	−16	−15
301	150	−44	+ 1	0
302	0	−14	+30	+30
327	0	−11	+ 3	0
335	40	−19	− 8	− 8

In this table, Column I gives the time in minutes during the run. Zero time is an arbitrarily chosen starting point and has nothing to do with the time that the membrane was first put into the electrolyte. Column II gives the pressure, in excess of atmospheric pressure, that was on the membrane when the readings were taken. Column III gives the actual potentials as measured. Columns IV and V give the change in potential from the last previous reading, a value in Column IV being the difference between a given reading in Column III and the one preceding it. Column V gives the differences that should be found, as calculated from Des Coudres' equation. A pressure increase of 5 cms. of mercury should make the cell potential one microvolt more negative. The first four readings given in the table show how the specific charge will vary over a period of time when, apparently, it should remain constant. Since, however, the response of potential to pressure change is almost instantaneous, while the specific charge varies more slowly, this difficulty is not serious. The table shows plainly that the measured potential is very exactly the sum of the membrane's specific charge and the added charge due to the pressure effect.

While the conditions in a Des Coudres cell are admittedly different from those of a Donnan equilibrium, nevertheless there is this similarity, which is both necessary and sufficient for any membrane potential—the conditions are different on the two sides of the membrane (For a complete résumé of the conditions of a Donnan equilibrium, see Donnan: Chemical Reviews, 1, 73 (1924)).

It seems quite probable that, in a Donnan equilibrium, the ions to which the membrane is impermeable affect the contact potential difference between the membrane and solution by adsorption on that side to which they are confined. Hence, the contact potential is different on the two sides and so there is a potential difference across the membrane which is an effect quite other than that due to the diffusion forces whose values Donnan[1] first calculated and which Loeb considered in his membrane potential measurements. It is quite probable that this specific effect may be so small in some cases, in comparison to the Donnan effect, that it may be ignored. However, as will be shown later, this specific effect is quite variable, and, under certain conditions, must be taken into account. If this is correct, it is easy to see why Prideaux, in plotting the data from his membrane potential measurements, obtained curves which had intercepts on the potential axis, instead of passing through the origin. This indicated a constant potential, algebraically additive to the Donnan effect investigated.

In the experiments in which gold-beaters' skin and parchment paper were used instead of collodion, difficulties were encountered which proved insurmountable. The gold-beaters' skin would not stand the pressure and the parchment paper seemed to react chemically with the electrolyte and turn pink after about two days. Only very erratic results were obtained with these two materials and hence no accurate pressure experiments were possible.

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[1] Z. Elektrochemie, 17, 572 (1911).

A Specific Charge Hypothesis

Bartell and Van Loo[1] have shown that collodion membranes are, in structure, simply sheets of impervious collodion penetrated by numerous small holes. These holes are formed by the evaporation of the volatile matter in the preparation of the membrane. Regulation of the extent of the evaporation regulates the size of the holes. If the evaporation continues until all the volatile matter is gone, the holes fill up and the membrane becomes impermeable. In our work this was found to be true, for such membranes, when placed in a circuit, made no electrical connection. Hence, all diffusion and ionic conduction take place through these capillary channels.

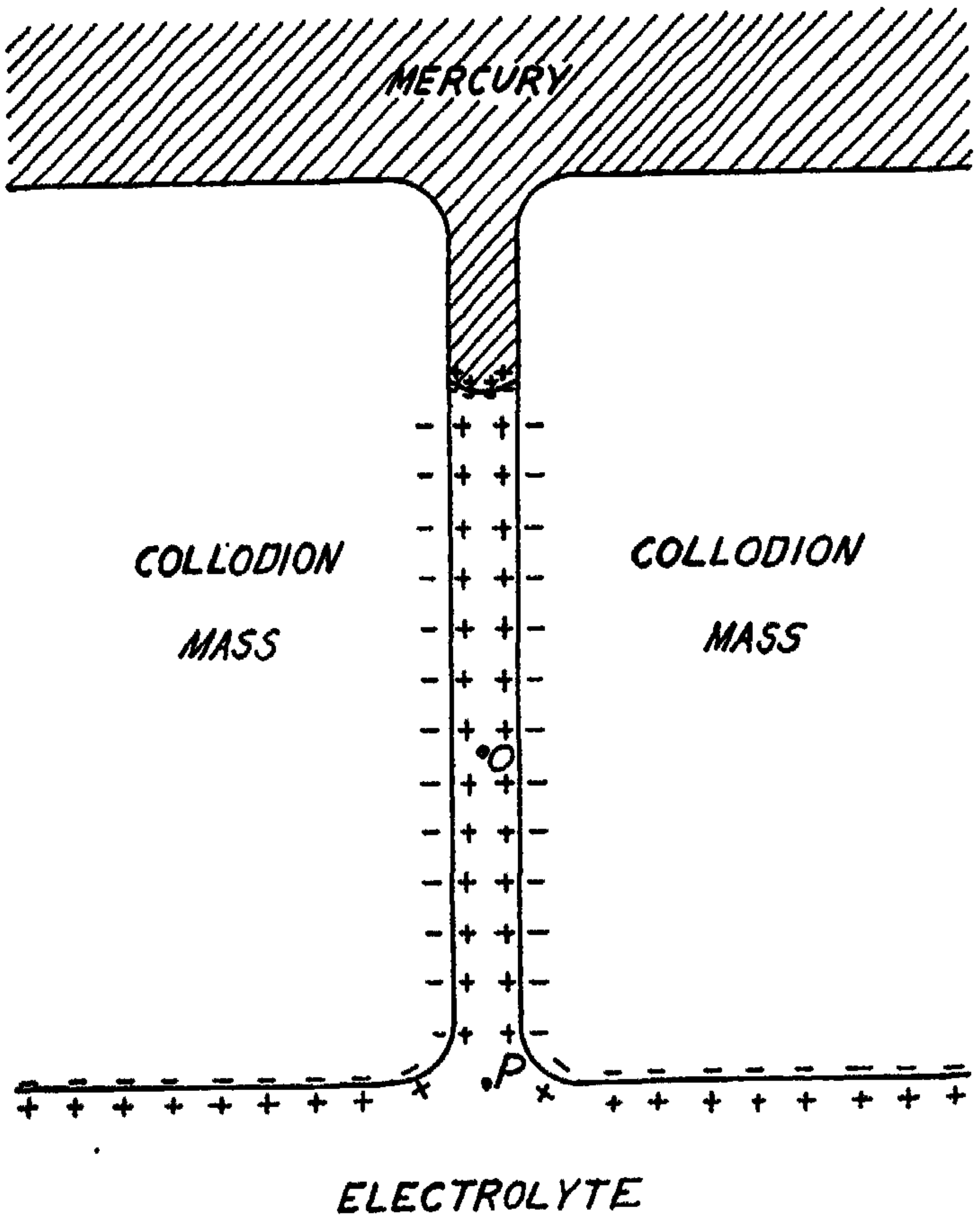

FIG. 2

Bartell and Van Loo present data showing the diameters of these holes for membranes ranging from "least permeable" to "very permeable." All

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[1] J. Phys. Chem., 28, 161 (1924).

diameters are of the order of magnitude of a micron. As the molecules of mercury are much smaller than the pore diameters, it seems reasonable to assume that the impermeability is due to negative capillary attraction, since mercury is depressed in a capillary tube We have, then, to consider a system of countless little tubes with mercury in one end.

Therefore, in the cell shown in Fig. 1, what is measured is the potential difference between the large mercury surface at the inside end of the tube K, and the countless little inverted mercury surfaces in the pores of the membrane. Since the large mercury surface is on the same level with the little surfaces, this potential difference should be zero, when the Hg pressure is atmospheric, if the membrane were ideal. But the membrane is not ideal for it is charged. This charge must affect the final equilibrium between the Hg^+ ions and these little surfaces. Hence the charge on these surfaces is not the same as that on the large surface at the inner end of K. The potential difference between H and K, then, is the "specific charge" as measured across the membrane.

In mounting the membranes, hot paraffin was poured into the space P in tube C. Since the membrane covered the hole O, the paraffin did not touch the electrolyte. There are, then, the following contacts in the cell: paraffin/membrane, paraffin/glass, membrane/glass, membrane/electrolyte, glass/electrolyte, mercury/membrane, mercury/glass, and mercury/electrolyte. According to Coehn and Franken there is a potential difference at all these contacts, due to differences in dielectric constants. But since the measurements were not made across many of these contacts, not all of them will have an appreciable effect on the readings. The contact with greatest effect on the values read is, of course, the mercury/electrolyte contact. It is only when other influences make the potential differences at this kind of contact in the membrane pores different from that at the same kind of contact at the inner end of the tube K that we get the potential difference which has been called here "specific charge." Of the other contacts, the influence of the membrane/electrolyte contact potential difference is probably the predominating one, although the mercury/membrane contact may also exert an appreciable effect.

An hypothesis will now be advanced to show how the membrane/electrolyte contact potential difference will influence the equilibrium between Hg^+ ions and the little mercury surfaces in the membrane pores, and thus give rise to a specific charge. Assume that the membrane is charged negatively and that, therefore, the electrolyte side of the double layer is charged positively and that H and K Fig. 1 are under atmospheric pressure. This condition is illustrated in Fig. 2, which represents one pore of the membrane with the mercury above it and the electrolyte below it, as they were in the cells used. The width of the pore is, however, exaggerated in this figure, for while the actual thickness of the collodion membranes was about 0.22 mm., the diameter of the pores was only of the order of magnitude of a micron.

Around the charges on each side of a double layer are electrical fields. The intensity of an electrical field is inversely proportional to the square of the distance from the charge. The two sides of a charged double layer do not coincide, but are spacially separated, although only a very small distance exists between them. The positive charges of the liquid side of the double layer are probably not all concentrated at one mathematical surface. Most likely they are spread out, making a zone of excess positive charges in which the excess gradually grows less as the distance from the membrane surface grows greater,[1] until the neutral conditon of the main bulk of the solution is reached. Hence, any point P, Fig. 2, just at the mouth of a pore, is a little closer to the positive charges of the liquid layer than to the negative charges on the collodion mass. Therefore, very close to the end of the pore the positive field from the charges on the liquid side of the double layer predominates to some extent. This must be so, since the distances are small and the positive charges are nearer and would tend to screen off the negative field of the relatively more distant negative charges on the collodion. Hence, if a negative charge were at the point, P, Fig. 2, it would be drawn into the pore. But if it were at the point O, there would be no unbalanced electrical fields acting upon it.

Now at the large mercury surface at the inner end of the tube K, Fig. 1, there exists the usual equilibrium between osmotic pressure and the opposing forces of the solution tension of mercury and the electrostatic force. At each of the mercury surfaces in the pores of the collodion the same forces are acting. The only difference here is, according to this hypothesis, that the concentration of the electrolyte within the pores must necessarily be different from that in the cell below. This difference arises as follows: When the membranes are first put into the cells, the pores are full of distilled water, but at once diffusion starts, to equalize the concentrations of solutes within and without the pores. In this case, the solutes are all electrolytes which dissociate and produce ions that diffuse. As each ion reaches the mouth of a pore, as at point P, Fig. 2, it is either drawn inward or repelled outward, according to whether it is negatively or positively charged. Hence when equilibrium is finally reached, the concentration within the pores is not the same as it would be if the pore walls were not charged. That is, the concentration of the Hg^+ ions, in the case assumed, would be less. For this reason, the positive charge at the little mercury surfaces in the pores would not be as great as the charge at the inner end of the tube K in Fig. 1. Therefore, when the cell potential is measured under these conditions, the little mercury surfaces appear to be charged negatively with respect to K, as indicated in Fig. 1, although for ordinary concentrations of Hg^+ ions, they are actually charged positively as indicated in Fig. 2. If, on the contrary, the charge on the collodion mass be assumed to be positive, the liquid layer would bear a negative charge. Then the Hg^+ ions would be attracted by the predominating negative field, which in this case would aid the osmotic pressure, and the concentration would be greater in the pores than outside. Hence the positive charge on

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[1] F. E. Burton: Colloid Symposium Monograph (1926).

the mercury surfaces in the pores would be greater than on the large open surface and the little mercury surfaces therefore appear to be charged positively, when the cell potential difference is measured. In either case, the specific charge as read, is the same in sign as the actual charge on the collodion mass, but of course, is different from it in magnitude. In other words, the specific charge as read is only the difference between two single electrode potentials which are different because the concentrations of the ions in contact with the electrodes are different, for the measurements are made through the pores and not across the collodion/electrolyte contact surface. That is, the specific charge "as read" is the potential reading at zero mercury pressure on the membrane. The actual specific charge would be the potential difference between the solid material of the membrane and the liquid in contact with it. No attempt was made to determine the quantitative relation between the specific charge as read and the actual charge of the membrane.

In the case of other membranes and equilibria in which the action may not take place altogether through holes, but perhaps somewhat through the membrane material, the specific charge must play a more important role. For then it adds more directly to the thermodynamic effect and not indirectly through its effect on another equilibrium.

Support is given to the hypothesis by the more recent work of L. Michaelis[1] and associates, who, in their studies of the permeability of membranes for electrolytes, find differences in the ionic mobilities of cations within and without the pores of dried collodion membranes that can be accounted for on the basis of the electrical effects within the capillaries. Further in the work of Mlle. Chaveraun[2] the selective permeability of gelatin membranes is accounted for by assuming a retardation of one kind of ions by the electrical charges covering the pore walls.

Specific Charge Data and Discussion

The effect of temperature on the specific charge as read is shown in Table II. These readings were also taken after the membranes had stood for over two weeks.

TABLE II

Effect of Temperature on Specific Charge

Temperature °C	I	II	III	IV
20	+15	+ 10	+ 2	+10
25	−74	−100	−40	−30
30	−98	−264	−90	−45

The data given in Columns I and II are from an electrolyte of 0.1 N $HgNO_3$ and 0.02 N HNO_3. This is about the weakest acid that will prevent hydrolysis and precipitation of the mercury salt. The two columns give data from two

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[1] L. Michaelis: J. Gen. Physiol., 8, 33-59; Michaelis and Perlzweig: 575-98; Michaelis, Ellsworth and Weech: 671-83; Michaelis, Weech and Yamatori: 685-701 (1925); Michaelis and Weech: 11, 147-58 (1927); 12, 55-81 (1928).

[2] Compt. rend., 185 502-5 (1927).

different runs made about a month apart with membranes from two different sources of collodion. The data in these columns show about the extent to which the results can be duplicated. The electrolyte from which the values in Column III were obtained was 0.1 N with respect to both $HgNO_3$ and HNO_3, while that which Column IV represents was 0.1 N $HgNO_3$ and 0.5 N HNO_3.

According to the above data, the higher the temperature the more negative the specific charge becomes. A few fluctuating readings from parchment paper and gold-beater's skin membranes indicated that the negative charge decreased at higher temperatures, as was the case with the collodion membranes in the strong acid electrolytes. Like the four cases shown in Table II, with most of the electrolytes used, a reversal of sign was observed at a temperature a little over 20°C. Little data on the effect of temperature has been published. Coehn and Franken observed a reversal of sign in the potential difference at the contact surface between paraffin and water. They found, however, that the paraffin became more positive the higher the temperature.

The change of the specific charge as the composition of the electrolyte is varied is shown in Table III. The various figures as arranged in this table are self-explanatory, and are the averages of many runs. The final values were taken at least three weeks and sometimes four weeks after the membranes first touched the electrolytes. The values used for averaging deviated on either side of the figure given about 20 per cent as a maximum, with the exception of those for the normal acid, which were erratic. The normal acid did, however, always cause the membrane to be charged positively at all temperatures investigated.

TABLE III

Effect of Composition of Electrolyte on Specific Charge at Zero Pressure and at 25°C

	Composition of Electrolyte in Normalities					
HNO_3	0.02	0.1	1.0	1.0	0.5	0.5
$HgNO_3$	0.1	0.1	0.1	0.1	0.01	0.5
Specific Charge in microvolts	−75	−40	−30	+350?	−35	−15

It is evident that varying the concentration of the electrolyte will doubtless change somewhat its dielectric constant. However, the effect on the extent of adsorption is the predominating factor here. This is clearly demonstrated in Table III. In every instance, the higher the concentration of H^+ or Hg^+ ions, the more positive or less negative is the membrane charge. When high enough, the negative charge which would be on the collodion due to the difference of dielectric constants is overcome and the sign reversed. This agrees with the results of other workers on many different materials.[1]

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[1] Perrin; Bartell and Hocker; Coehn and Franken: loc. cit.

The changing of the charges over a period of time is shown in the curve in Fig. 3. Because of the rapid changes, measurements soon after the membrane first touched the electrolyte were hard to make. For this reason, the values given for this period are not very accurate, and the curve simply shows the general trend. In all cases, the charge as measured at the start was negative. This is because the pores of the collodion membrane are filled with water at first, and hence the single electrode potential common to all the little mercury surfaces in these pores is not nearly so positive as the single electrode potential of the surface at the inner end of the tube K in Fig. 1.

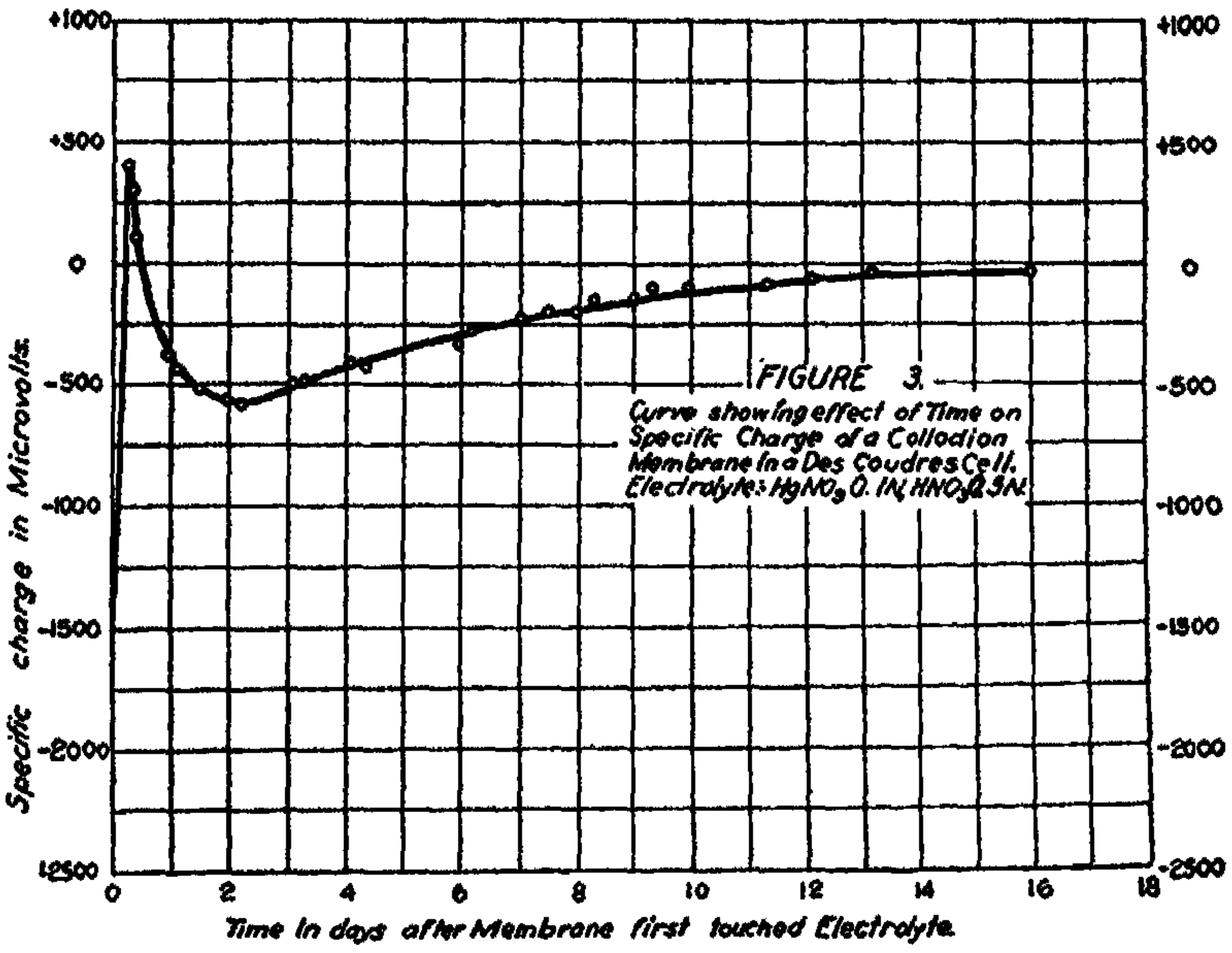

Fig. 3

When the membrane comes into contact with the electrolyte, diffusion begins to equalize the composition of the liquid in the pores with that of the electrolyte below them. Because of the fast moving H^+ ions, there is set up a boundary potential which is in opposition to the first mentioned negative effect. Then, also, as the Hg^+ ions diffuse into the pores, they deposit on the mercury surfaces and begin to equalize the two mercury-surface potentials. Soon, because of these two latter effects, the sign of the apparent charge is reversed. As the acid concentration becomes equalized within and without the pores, the positive boundary potential decreases. Hence, the curve soon passes through a maximum, begins to fall, and soon again goes through zero. The diffusion of the $HgNO_3$ will, of course, tend to create a boundary potential also, but this effect is masked by the larger one due to the rapidly moving H^+ ion. It is the net boundary potential which helps to bring about this temporary reversal in sign.

When the net boundary potential almost ceases to exist, the curve no longer continues to fall but passes through a minimum, and then rises again. The original negative charge on the collodion mass due to the difference of dielectric constants, has from the start been gradually reduced by adsorption of positive ions. This negative charge has retarded the entrance of Hg^+ ions into the pores and assisted the anions, because of the positive field due to the positively charged liquid side of the double layer. Since this influence is now decreasing, more Hg^+ ions can now get into the pores and deposit on the mercury surfaces. Hence the difference between the charge on these surfaces and that on the surface at the inner end of the tube K in Fig. 1, is steadily decreasing, and the curve rises towards zero, until equilibrium is reached between the combined effects of the solution tension of mercury, the electrostatic force at the mercury/electrolyte contacts in the pores, and the osmotic pressure of the Hg^+ ions corresponding to the concentration of $HgNO_3$ within the pores, which is modified by the electrical fields of the double layers of the collodion/electrolyte contact, as described in the discussion of the hypothesis above. As the curve shows, over two weeks must elapse after the membrane first touches the electrolyte before the specific charge becomes really constant. All values given in the tables above were read after the final equilibrium was reached and the curve had become practically horizontal.

As far as could be found, little similar data have been published showing the effect of time on the membrane charge. As stated above, the actual values of the specific charge as read in this cell are not the same as the charges existing on the membranes. These curves do, however, show qualitatively the effect of time on the actual membrane charge. The effect of time on boundary or diffusion potentials has, of course, been observed and recorded before. Lewis and Rupert,[1] in working with liquid junctions, found that equilibrium was established in twenty-four hours. They observed a maximum change in potential difference of about 0.8 of a millivolt, without, of course, any reversal in sign. Cumming and Gilchrist[2] in making observations on cotton wool boundaries for twenty-four hour periods, found diffusion to be practically complete in six hours. They recorded no reversal in sign.

In using several kinds of membranes at the boundary A in the following chain

$$\underset{}{1.0\text{ N KCl}}\,/\,\underset{A}{}0.1\text{ N HCl}\,/\,\underset{B}{}1.0\text{ N KCl}$$

with only the liquid junction at B, they observed in most cases that the potential of the chain fell steadily to zero in twenty-six hours Lewis and his students[3] using the "Sandfüllung" of Bjerrum[4] which was simply a layer

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[1] J. Am. Chem. Soc., 33, 299 (1911).

[2] Trans. Faraday Soc., 9, 174 (1913).

[3] Lewis, Brighton and Sebastian: J. Am. Chem. Soc., 39, 2245 (1917).

[4] Z. physik. Chem., 53, 428 (1905).

of sand in which the two liquids of different concentrations met, found at first the surprisingly high potential difference of 0.03 volt which—"fell rapidly without reaching any definite limiting value." The comparatively high initial potential difference and the rapid fall are similar to our own results.

Summary

1. An investigation of the Des Coudres cell was made under different conditions.

2. The membranes used in this cell were found to be specifically charged even when no pressure was placed upon them.

3. As the result of specific charges, the cell potentials as read did not agree with the values calculated from Des Coudres' equation.

4. It was found that within the limits of experimental error, the cell potentials were the algebraic sum of the specific charges and the calculated values.

5. The effects of temperature, composition of electrolyte, nature of the membrane, and the period of time after exposing the membrane to the electrolyte, on the specific charge of membranes in a Des Coudres cell were studied.

6. In a Des Coudres cell, it was assumed that the actual potential difference between the membrane and electrolyte indirectly affected the measured potential. This indirect effect (the specific charge) was assumed to be due to the action of the electrical field around the charged double layer at the contact surface of electrolyte and membrane. It was assumed that the field of the liquid layer predominated over the field due to the charge on the collodion mass and aided or opposed the osmotic pressure in its tendency to cause diffusion of the ions into the pores. This, it was assumed, makes the concentrations of electrolytes in the pores of membranes different from that in solutions in contact with them. Therefore, the single electrode potential at the surface of mercury in pores will be different from that at an open surface. The cell potentials were read between a number of such surfaces within pores and a large open surface and this difference of potential existing at zero pressure was called the "specific charge."

7. If, in other equilibria, the membrane potential measurements were made through the mass of the membrane instead of through holes, the specific charge would be more nearly, if not exactly, the same as the difference between the contact potential differences on the two sides of the membrane.

8. It has been pointed out that the specific charges of the membranes should be taken into consideration in measurements of membrane potentials.

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THE SORPTION OF SULPHUR DIOXIDE, CARBON DIOXIDE, AND NITROUS OXIDE BY ACTIVATED CARBON

BY D. O. SHIELS

Introduction

In view of the probability that adsorption or sorption of a gas by a solid adsorbent depends very largely on the stray field of force about the molecule, or in other words on secondary valence forces of the molecule of gas, it was considered advisable to investigate the adsorption or sorption of gases which have a very similar electronic configuration and in which the secondary valence forces, as judged by critical temperature, surface tension in liquid state, etc., are very similar. The gases selected were carbon dioxide and nitrous oxide.

In addition the sorption of sulphur dioxide was measured, as this gas has a much higher critical temperature, and it was thought that a comparison of the sorption isotherm of this gas with those of the first two gases mentioned would be interesting.

Table I shows some of the physical constants of the gases concerned—

TABLE I

	C.P.	C.T.	Viscosity 20°C
N_2O	75	35.0°C	148×10^{-6}
CO_2	77	31.2°C	148×10^{-6}
SO_2	78.9	155.4°C	

When this work was commenced (November, 1926) no other work had been published in which the adsorption of carbon dioxide and nitrous oxide by activated charcoal had been compared, although this had been done for the adsorption of these gases by silica gel (see Patrick, Preston and Owens.)[1]

Subsequently to the carrying out of the experimental part of this investigation Gregg[2] has published an extensive investigation into the heats of adsorption of carbon dioxide, nitrous oxide, sulphur dioxide and other gases by activated charcoal in which the isotherms have been determined as well as the heats of adsorption.

The Apparatus and Method of Experiment

These were very similar to those used for the sorption of sulphur dioxide by platinised asbestos.

The activated carbon was contained in the glass container C (Fig. 1), the volume of which was determined by weighing the amount of water it contained.

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[1] J. Phys. Chem., 29, 421 (1925).

[2] J. Chem. Soc., 1927, 1494.

This was connected by means of the ground joint and tap T_1 with the reservoir R, the volume of which between T_3, T_1 was also determined as above.

To R was attached a mercury manometer M_1 and McLeod gauge G.

Between this part of the apparatus and the part which supplied the respective gases were two drying tubes D_1 and D_2 in series containing Merck's phosphorus pentoxide.

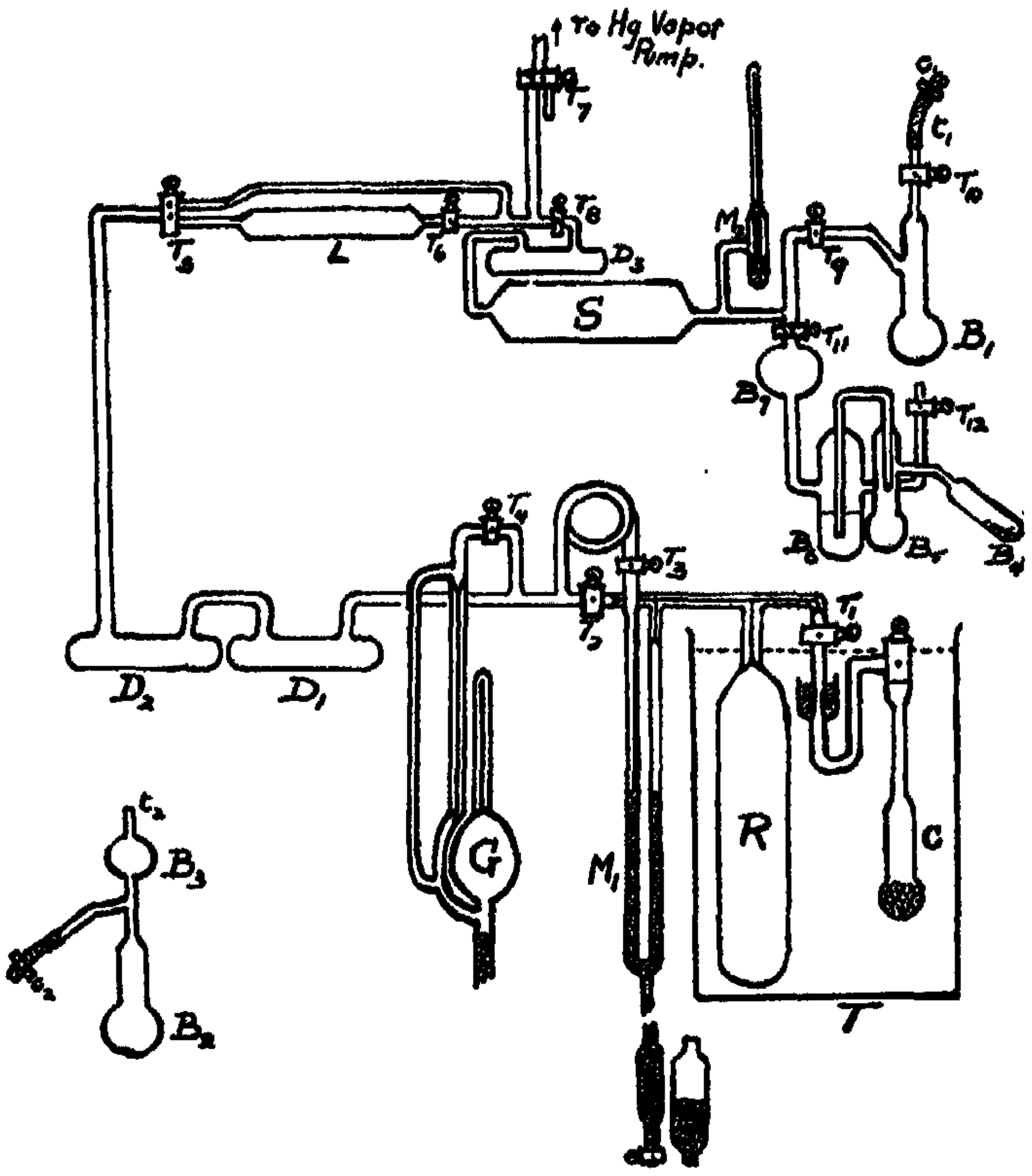

FIG. 1

The whole of the apparatus could be evacuated by the mercury vapor diffusion pump backed by water pump.

The sulphur dioxide was prepared in same way as in the case of the platinised asbestos experiments.

Carbon dioxide was prepared in a similar way but by using Merck's pure sodium carbonate instead of sodium sulphite.

Nitrous oxide was prepared in the following way. Crystals of the pure salt were placed in bulb B4 which was then fused to the bulb B5. The whole apparatus was then evacuated to low pressure. A strong solution of pure ferrous sulphate from which the oxygen and nitrogen had been boiled out under vacuum was introduced through T_{12}, allowing some of the solution to remain above the tap, so as to prevent the egress of any air to the apparatus. The apparatus was further evacuated to very low pressure. The pump was then shut off and the ammonium nitrate gently heated to decomposition. The ferrous sulphate absorbed any nitric oxide and a supply of pure nitrous oxide was obtained in the reservoir S. This was in connection with a drying tube D_3 containing Merck's phosphorus pentoxide. The tube L was packed with soda lime and was used to absorb sulphur dioxide as much as possible before using the pump, so as to prevent as far as possible corrosion of the iron mercury vapour pump.

Activated Carbon

This was obtained from a German gas mask and was graded to 12-14 mesh. It was extracted by repeated boiling with concentrated hydrochloric acid and subsequent washing in boiling distilled water until the washings showed no trace of chloride when tested with silver nitrate.

The ash content was reduced by this means from 12.9% to less than 0.1%.

The volume of free space in the container when the activated charcoal was present was determined in the following way.

The density of the evacuated charcoal was determined by taking a known weight and evacuating it at 270°C to low pressure and then allowing water at known temperature to enter the container and completely fill the free space. From the weight of water its volume could be obtained and, knowing the total internal volume of the container, the volume of the evacuated charcoal was obtained and hence its density.

From a knowledge of the weight of the evacuated charcoal used in an adsorption experiment and its density its volume could be calculated and hence the volume of the free space with the charcoal present in the container.

Method of Determining Adsorption

The charcoal was first of all evacuated, and heated, the details of the process being given later.

After evacuation of the charcoal the furnace was removed and a large beaker placed around C and the reservoir R to act as a thermostat. The temperature of the water in the thermostat was maintained constant to $\pm 0.03°C$ by a gas thermo-regulator and small stirrer driven by electric motor.

With tap T_1 shut, the gas for which the isotherm was being determined was allowed to enter R to a convenient pressure and then T_2 was shut.

After allowing time for the gas to come to temperature equilibrium the pressure was read to 0.01 m.m. by means of a travelling microscope mounted on a thick glass plate resting on a solid wooden foundation.

T_1 was then opened and the charcoal allowed to adsorb the gas. The pressure was read at intervals until it remained constant to within 0.02 m.m. for 20 minute period.

From a knowledge of the volumes of the vessel C and the connecting tube up to Tap T_1, of the reservoir R from T_1 to a mark on the manometer tube, and of the manometer tube per cm. length, the volume of gas adsorbed could be readily calculated.

A similar process was gone through for the desorption experiments, but in these cases the vessel C containing a known pressure of gas was exposed to the completely evacuated reservoir R and then the equilibrium pressure in C and R measured.

Preliminary Evacuation of Charcoal

The sorption isotherm of SO_2 was determined first. The charcoal was evacuated to 4×10^{-4} m.m. pressure in the cold, and then heating was commenced. The evacuation at 270-300°C was continued for one hour, at the end of which the pressure was 1.6×10^{-2} m.m. The pump was left running during the cooling, the final pressure at the end of a further half hour being 1.5×10^{-3} m.m.

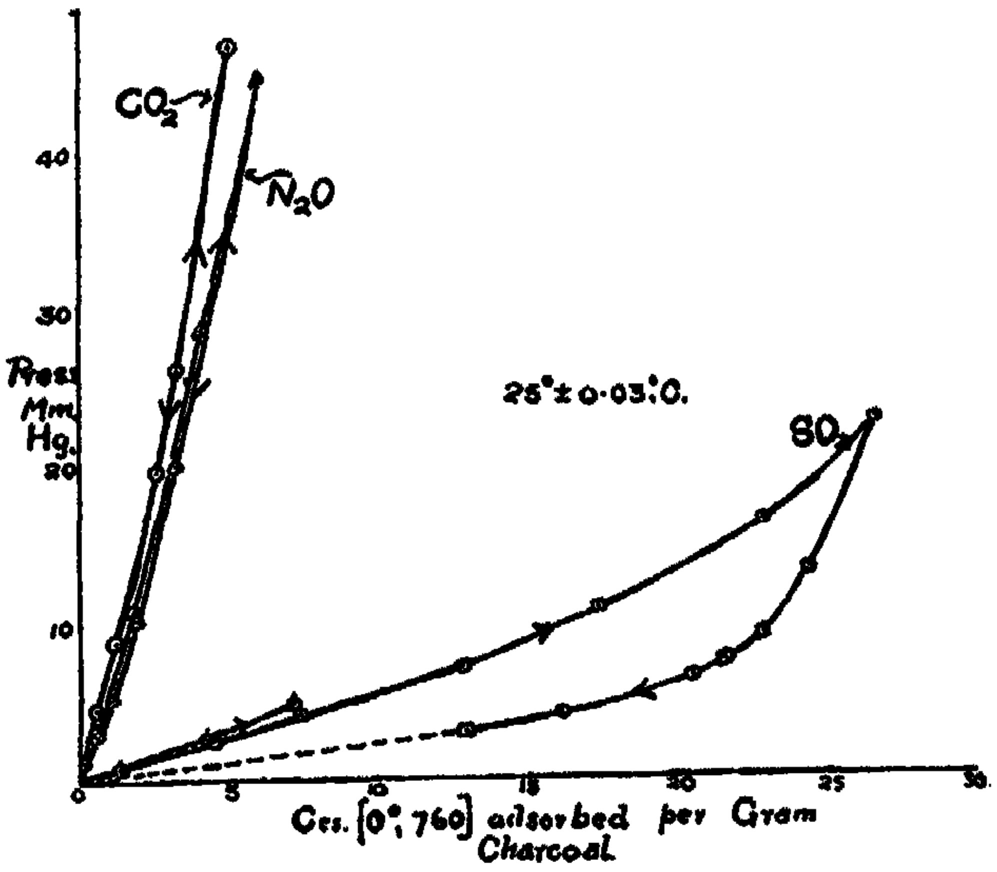

FIG. 2

The charcoal was then allowed to adsorb SO_2, but there was apparently a leak, and so the evacuation was repeated.

After evacuation for 1 hour 12 mins. at 300°C the pressure was 2×10^{-3} m.m.

Adsorption experiments were carried out, and then the desorption.

C was then evacuated at 25° for 1 hour.

In another hour the amount of gas evolved was 0.084 ccs.

The charcoal was then heated to 270°C for an hour and evacuated to 1.3×10^{-3} m.m. The second adsorption experiments were then carried out. (Table IIb).

The charcoal was then accidentally exposed for a few seconds to a pressure of about 10 cms. of air. It was then evacuated at 300°C for 1½ hours and for 1/2 hour during cooling the final pressure being 1.2×10^{-3} m.m.

The experiments with CO_2 were then carried out. The charcoal was then evacuated at 300°C for 1½ hours, the pressure finally being 1.3×10^{-3} m.m. while charcoal was still hot.

The experiments with N_2O were then carried out. The heating was done by means of a small electric furnace placed around the container C.

The results are tabulated in Table II.

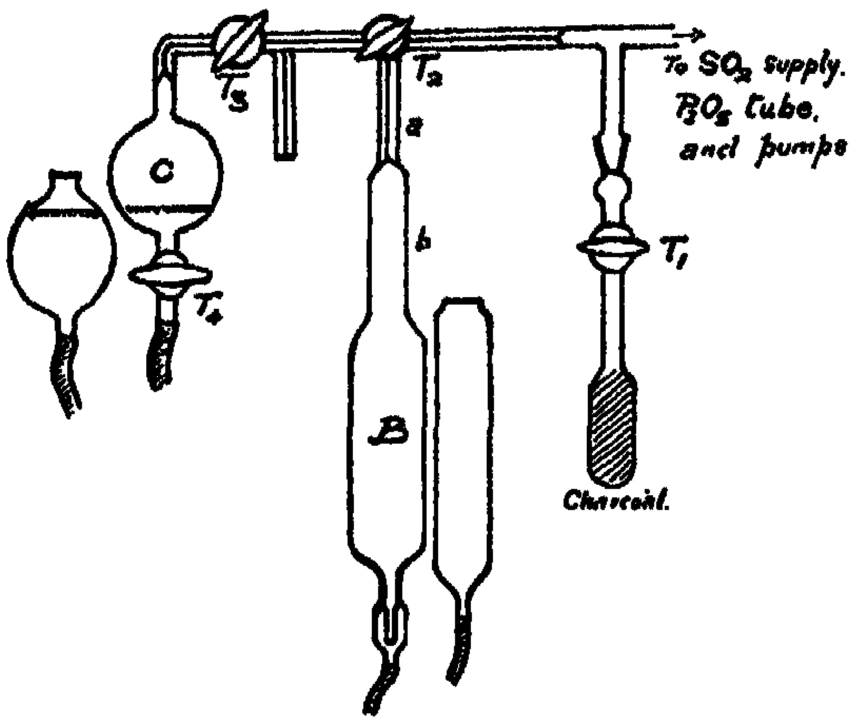

FIG. 3

TABLE II

Temperature 25°C. Pressure in m.m. Hg = p. ccs. at N.T.P. per gram of charcoal = q

	SO_2		CO_2		N_2O	
	p	q	p	q	p	q
(a)	2.39	4.467	8.86	1.33	3.26	0.52
	4.12	7.36	26.04	3.32	10.58	1.76
	7.035	12.79	46.43	5.15	28.62	4.17
	10.75	17.30	19.57	2.93	44.80	6.02
	16.20	22.81	8.86	1.29	20.01	3.23
	22.67	26.50	4.39	0.64	10.00	1.75
	13.06	24.44			4.95	1.02
	9.03	22.92			2.82	0.58
	7.50	21.60			1.12	0.14
	6.32	20.47				
	4.00	16.16				
	2.93	12.98				
(b)	0.385	1.349				
	2.67	4.171				
	4.90	7.181				

Discussion

From the isotherms plotted in Fig. 2 it will be observed that the amounts adsorbed at any given pressure are in the order of the respective Critical Temperatures, and that in the case of CO_2 there is practically no hysteresis, the sorption and desorption curves practically coinciding.

In the case of N_2O there is definite though small hysteresis, whereas in the case of SO_2 the hysteresis is very marked.

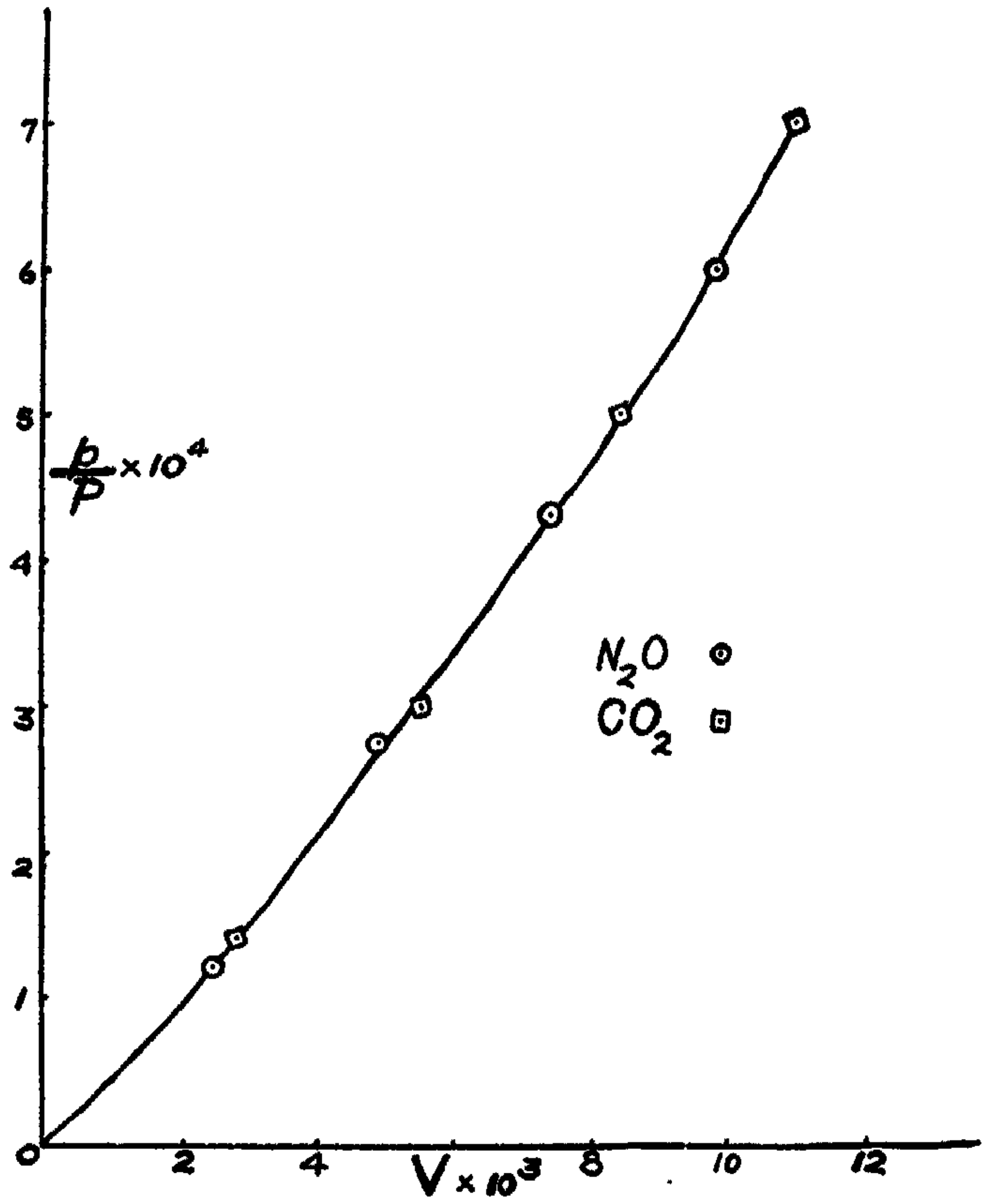

FIG. 4

Furthermore, the isotherms for CO_2 and N_2O very nearly coincide, as had been anticipated.

If instead of plotting p against volume of gas adsorbed the expression p/P is plotted against V, the volume of liquid adsorbed, where p is the observed equilibrium pressure during adsorption, and P is the saturation pressure at 25°C, the curves for CO_2 and N_2O coincide.

That for SO_2 however does not come near the common curve for the other two gases.

In the case of the adsorption of SO_2 by silica gel Patrick and McGavack[1] have shown that the plot of log ($p\sigma/P$) against log V (where σ = surface tension) gives a straight line, the same curve serving for the adsorption at all temperatures.

TABLE III

p = Equilibrium pressure in m.m. of mercury.
q = ccs. of gas at N.T.P. per gram of charcoal.
P = Saturation pressure at 25°C.
V = Volume of liquid adsorbed per gram of charcoal.
σ = Surface tension of adsorbate in liquid state.
D = Density of liquid at 25°C.

	p	q	p/P	V	$p\sigma/P$	
CO_2	7	1	0.0_3140	$.0_22807$	$.0_435$	D = 0.70
	15	2	0.0_3301	$.0_25614$	$.0_475$	P = 49.800 m.m.
	23.8	3	0.0_3478	$.0_28421$	$.0_3119$	σ = 0.25 dynes/cm.
	34.3	4	0.0_36887	.01123	$.0_3172$	(above at 25°C)
N_2O	5.5	1	0.0_3118	0.0_2247	0.0_3208	D = 0.796
	13	2	0.0_3275	0.0_2494	0.0_3484	P = 46.500 m.m.
	20	3	0.0_343	0.0_2741	0.0_3757	σ = 1.75 dynes/cm.
	28	4	0.0_360	0.0_2988	0.0_2106	(above at 25°C)
SO_2	2.7	5	0.0_470	0.01068	0.0_2166	D = 1.3695
	5.5	10	0.0_3143	0.02137	0.0_2338	P = 38,500 m.m.
	9.0	15	0.0_3234	0.03205	0.0_2553	σ = 23.6 dynes/cm.
	13.2	20	0.0_3344	0.04274	0.0_2811	(above at 25°C)
	19.6	25	0.0_3510	0.05342	0.0120	

	Log (p/P)	Log V	Log ($p\sigma/P$)
CO_2	$\bar{4}.1462$	$\bar{3}.4486$	$\bar{5}.5443$
	$\bar{4}.4788$	$\bar{3}.7493$	$\bar{5}.8750$
	$\bar{4}.6794$	$\bar{3}.9255$	$\bar{4}.0757$
	$\bar{4}.8381$	$\bar{2}.0424$	$\bar{4}.2356$
N_2O	$\bar{4}.0726$	$\bar{3}.3930$	$\bar{4}.3180$
	$\bar{4}.4397$	$\bar{3}.6940$	$\bar{4}.6845$
	$\bar{4}.6334$	$\bar{3}.8697$	$\bar{4}.8787$
	$\bar{4}.7796$	$\bar{3}.995$	$\bar{3}.0250$
SO_2	$\bar{5}.8470$	$\bar{2}.0287$	$\bar{3}.2197$
	$\bar{4}.1552$	$\bar{2}.3300$	$\bar{3}.5282$
	$\bar{4}.3692$	$\bar{2}.5060$	$\bar{3}.7425$
	$\bar{4}.5362$		$\bar{3}.9095$
	$\bar{4}.7080$	$\bar{2}.7280$	$\bar{2}.0806$

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

Log (p/P) against log V gives straight lines, the curves for different temperatures converging towards the region where p/P = 1.

Patrick, Preston and Owens have also shown that in the adsorption of CO_2, N_2O, by silica gel log (pσ/P) plotted against log V gives straight lines, the lines for different temperatures being parallel to each other and those for CO_2 being parallel to those for N_2O.

If, however, the value of σ was corrected for the influence of the radius of curvature on the surface tension it was found that the log V/(pσ/P) curves for N_2O at 0°, 20°, 30° coincided, and those for 0° and 20° for CO_2 coincided with each other but not with those for N_2O. Apparently the sample of gel used for the experiments with CO_2 at 0° and 20° was different from that used for N_2O, the water contents being 1.28% and 1.38% respectively although the authors state that the endeavour was to have the same samples or portions of the same samples used throughout. They do not make this point quite clear.

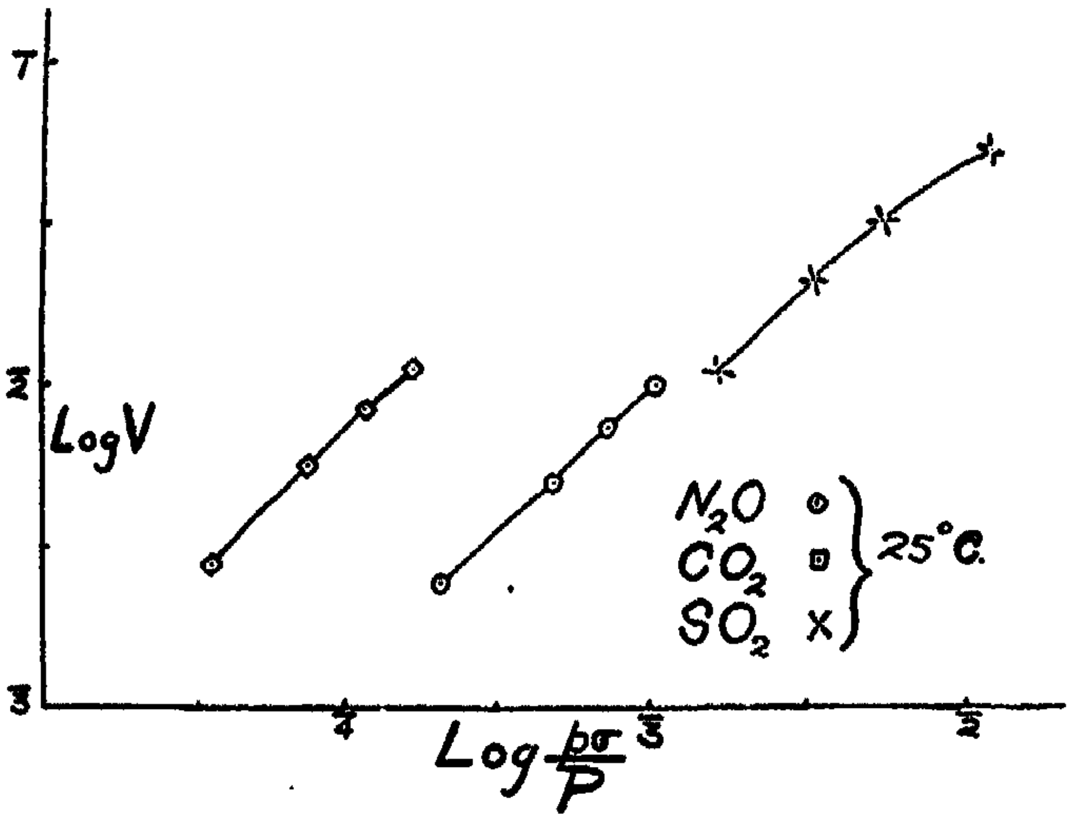

Fig. 5

In calculating the values of p/P, V, pσ/P the values of V have been determined from the weights of the gases adsorbed and the densities of the substances in the liquid condition at 25°C.

The densities of CO_2 and N_2O have been obtained from curves drawn from the data of Patrick, Preston and Owens.

The values of P and of σ have also been obtained in the same way from their data. The value of σ for CO_2 at 25°C is somewhat uncertain.

The density of liquid SO_2 at 25° has been obtained from Lange's values in Landolt-Bornstein's Tabellen. The value of P for SO_2 has also been obtained from Landolt-Börnstein's Tabellen and the value of σ for SO_2 from a curve drawn from data of McGavack and Patrick.

Table III gives the values of the different quantities mentioned.

In the present investigation the p/P, V curves for CO_2 and N_2O coincide exactly, therefore also the log (p/P), log V curves.

The fact that the log (p/P), log V curve is a straight line indicates that the isotherm may be represented by an equation of the form.

$V = K(p/P)^{1/n}$ which is a modified form[1] of Freundlich's well-known equation.

If the surface tension factor be introduced as in the case of the investigations previously quoted the log V, log $(p\sigma/P)$ curves for CO_2 and N_2O are parallel straight lines and that for SO_2 is, over most of the range considered, a straight line parallel to the other two curves.

The exact coincidence of the log V, log (p/P) curves for carbon dioxide and nitrous oxide, and the lack of such coincidence when the log V, log $(p\sigma/P)$ curves are plotted may indicate that the introduction of the surface tension factor σ is not warranted, or that the value used may be incorrect. The latter possibility is very probable, since one would anticipate that these two substances would have very nearly the same values for their surface tensions, whereas the values used are quite different. (Table III).

It is interesting to note that if the gases experimented with are arranged in order according to the volumes adsorbed at any particular temperature, the order is N_2O, CO_2, SO_2 for silica gel[2] and also for glass,[3] whereas in the case of activated charcoal it is CO_2, N_2O, SO_2.

The values of K and 1/n for carbon dioxide and nitrous oxide have been determined from the curves. K is taken as the value of V when $p\sigma/P = 1$.

The values for SO_2 have not been calculated since the curve is straight over such a small range that extrapolation is not justified. These values are compared with those obtained for silica gel by Patrick, Preston and Owens.

TABLE IV

Gas	Silica Gel	Charcoal	Silica Gel$^{1/n}$	Charcoal
CO_2	0.145*	28.17	0.866*	0.909
	0.558†		0.898†	
N_2O		3.98	0.891*	0.875

* These values for silica gel are at 0°C.
† These values for silica gel are at 20°C.

It appears that the value of n is characteristic of the gas whereas K depends on the nature of the adsorbent.

Hysteresis

It will be observed that in the case of N_2O and SO_2 the pressure corresponding to a definite quantity of gas adsorbed is greater when the point is approached from a lower pressure than it is when approached from a higher pressure. This phenomenon of hysteresis has been previously observed by

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

[2] Patrick, Preston and Owens: J. Phys. Chem., 29, 421 (1925).

[3] Bangham and Burt: Proc. Roy. Soc., 105A, 481 (1924).

a number of investigators. The explanation frequently given in the case of the adsorption of gases is that it is due to less condensible gases which are turned out by the more strongly adsorbed gas, but apparently no attempt has been made until recently to analyse the gas in contact with the solid adsorbent to see if it contains any gas other than that used as the adsorbate. In considering hysteresis it is important that particular attention be given to the conditions of the preliminary evacuation of the adsorbent and its history during experimental work.

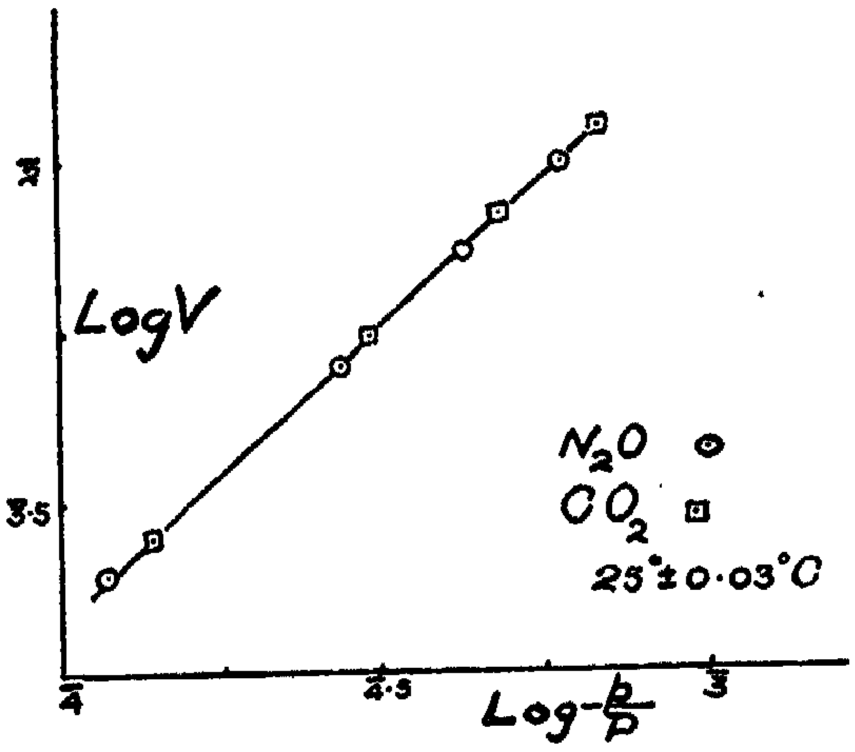

FIG. 6

Richardson[1] has shown that in the adsorption of carbon dioxide by activated cocoanut charcoal hysteresis occurs, but that the effect disappears at temperatures above 55°C.

McGavack and Patrick, in their work on adsorption of sulphur dioxide by silica gel, have shown that after ordinary evacuation of the gel the adsorption isotherms showed hysteresis, whereas if the gel was allowed to stand in contact with sulphur dioxide overnight, then evacuated, and the process repeated four times, the process of adsorption was reversible.

Gregg[2] states that in the adsorption of SO_2, CO_2, N_2O and other gases by charcoal hysteresis was due to the presence of non-condensible gases in the system. When the gas to be adsorbed was liquified and then distilled in high vacuum, and when the charcoal was thoroughly evacuated the sorption and desorption curves could be made to agree. However, a careful examination of their tabulated results shows that hysteresis was present in the case of nitrous oxide and sulphur dioxide at 40.35°C even when the gases were carefully purified as above.

It appeared from the experimental history of the charcoal used in the author's work, and the incidence of hysteresis, that the phenomenon did not

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

[2] J. Chem. Soc., 1927, 1494.

depend merely on the presence of "foreign" gases in the adsorbent. Table V may indicate this more clearly.

TABLE V

Adsorbate	Critical Temperature	Hysteresis	Temperature of Experiment
CO_2	31.2°C	None	25°C
N_2O	35.0	Slight	"
SO_2	155.4	Large	"

The order in which the gases were used was SO_2, SO_2, N_2O.

The history of the charcoal shows that it was "washed out" once with SO_2 and then the first adsorption curve and the desorption curve were determined. The second adsorption curve was then obtained. Only three points were determined on this; they lie very nearly on the first adsorption curve and show no indication of any tendency to approach closer to the desorption curve, as would be the case if less condensible gases were being removed.

The charcoal was then accidentally exposed to a pressure of 10 cms. of air for a few seconds. The amount of air adsorbed at 10 cms. pressure would probably be of the order of 0.7-0.8 ccs. per gram of charcoal. The weight of charcoal being 0.65 gram this would give about 0.5 ccs. of gas adsorbed. This would apply in the case of fresh charcoal exposed to air. In the present case sulphur dioxide was present to a pressure of several millimetres, and the quantity of air adsorbed would probably be less than the above estimate. The charcoal was then evacuated at 300°C for 1½ hours and then the carbon dioxide experiments were done. At the conclusion of the desorption experiments the charcoal was again evacuated at 300°C for 1½ hours and then the experiments with nitrous oxide were carried out.

In order to test whether the hysteresis was due to the liberation from the charcoal of less readily condensible gases owing to the adsorption of sulphur dioxide a fresh portion of the same sample of charcoal was taken and exposed to sulphur dioxide in the apparatus[1] shown in Fig. 3.

The charcoal was evacuated while cold to 1×10^{-2} m.m. and then heated to 200°C and evacuated during one hour at this temperature. The final pressure at room temperature was 2×10^{-4} m.m. The temperature used was lower than that previously used and the evacuation might thus be expected to be less complete.

It was then exposed to a pressure of 4 cms. of pure dry sulphur dioxide. After standing in contact with the charcoal at room temperature for 1/2 hour a sample of the gas which then had a pressure of 0.7 cms. was pumped off into the burette B. The whole of this apparatus up to T_3 had also been previously evacuated to 9×10^{-3} m.m. The absorbing vessel C was filled with an aqueous solution of iodine in potassium iodide.

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[1] Low: J. Soc. Chem. Ind., 41, 1 (1922).

By raising the mercury in B the gas was pumped via the three-way taps T_2 and T_3 into C. Absorption of the gas was practically complete, only a minute trace of gas being unabsorbed.

The liquid in C was originally in equilibrium with the oxygen and nitrogen and carbon dioxide in the air.

Assuming that the oxygen and nitrogen adsorbed by the charcoal when in contact with air are adsorbed in the same proportions as they exist in air, and that the traces which might be left on the charcoal after heating and evacuation, and which might subsequently be displaced by sulphur dioxide during adsorption of the latter would also be in the same ratio, adjustment of the level of the mercury in B ensured that this condition held at the conclusion of the adsorption of the sulphur dioxide in the absorbing liquid.

The result showed that in all probability if any less condensible gas or gases were turned out from the charcoal by the adsorbed sulphur dioxide neither oxygen or nitrogen were concerned.

Owing to the high solubility of carbon dioxide in water the possibility remained that carbon dioxide occurred in the sulphur dioxide after exposure to the charcoal, but was dissolved in the absorbing liquid.

There was no opportunity to make a thorough investigation on this question of hysteresis.

Summary

The adsorption of carbon dioxide, nitrous oxide, and sulphur dioxide by German activated gas-mask charcoal at 25°C has been determined from 0 to 40 m.m. pressure for the first two gases, and from 0 to 22 m.m. pressure for the last.

The adsorption process is reversible in the case of carbon dioxide.

In the cases of nitrous oxide and sulphur dioxide hysteresis occurs.

The log V, log p/P curves for carbon dioxide and nitrous oxide coincide.

The log V, log $p\sigma/P$ curves for the first two gases are parallel straight lines, that for sulphur dioxide being straight for part of the range considered and parallel to the other two.

The adsorption of nitrous oxide and carbon dioxide may be represented by Patrick's equation $V = K(p/P)^{1/n}$.

Acknowledgment

The experimental part of this work, with the exception of that on the analysis of the gases, was carried out during the period November 1926 to January 1927 at the University of Tasmania, and the author's thanks are due to Professor A. L. McAulay for facilities for the work. The author's thanks are due to Professor E. J. Hartung, D.Sc., for facilities for carrying out the gas analysis.

Chemistry Department,
University of Melbourne,
Feb. 12, 1929.

THE ADSORPTION OF MERCURY VAPOUR BY ACTIVATED CHARCOAL

BY D. O. SHIELS

Introduction

Apparently little work has been done on the adsorption of mercury vapour by activated charcoal, although it is of the first importance to know whether charcoal does adsorb mercury vapour or not, as it is usual in experiments on the adsorption of gases or vapours to measure the pressure by means of mercury manometers, and to use McLeod gauges containing mercury for the measurement of the pressure during evacuation of the charcoals previous to adsorption.

Apparently it has usually been assumed that at ordinary room temperature the adsorption would be very slight owing to the very low (0.001 m.m.) vapour pressure of mercury at this temperature.

Recently Zelinsky and Rakusin[1] have carried out experiments which appear to show definite adsorption of mercury vapour by activated birchwood charcoal.

An increase of weight equivalent to 5.63% of the weight of the charcoal was obtained by exposing it to mercury vapour at ordinary temperature. An increase equivalent to 4.65% of the weight of the charcoal still remained after exposure to an atmosphere free from mercury vapour.

Their method was to expose the charcoal in a dish to the vapour of mercury at room temperature, the dish containing the charcoal and a dish containing mercury being kept in a desiccator without any drying agent.

As considerable experimental work in adsorption of gases and vapours had shown no evidence of the adsorption of mercury by activated charcoal except in the slightest traces, and as the method adopted by the above authors is open to the objection that blank experiments were not done and the carbon may not have been in equilibrium with the water vapour in the atmosphere, it was decided to carry out experiments in a vacuum. While this work was in progress (August 1927) a paper by Coolidge[2] appeared, in which he showed that the adsorption of mercury vapour by activated charcoal was very slight at room temperature (0.3 mgr. per gram of charcoal at 20°C).

Experimental Details

The charcoal was a German gas-mask charcoal which had been extracted with concentrated hydrochloric acid, and then washed acid free. It had an ash content of less than 0.1%.

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[1] Ber., 59, 2072 (1926).

[2] J. Am. Chem. Soc., 49, 1949 (1927).

It was contained in a glass vessel C having a good vacuum tap, and could be attached by means of a ground joint to a bulb containing mercury, phosphorus pentoxide drying tubes, McLeod gauge and mercury vapour pumps.

The charcoal was evacuated to 6.7 × 10^{-5} m.m. while cold and then the temperature was raised to 400°C. The evacuation was continued for 1½ hours at this temperature and then the charcoal was allowed to cool off with the pumps running.

The final pressure at 200°C was 6.7 × 10^{-6} m.m. The container was then shut off, detached and weighed. The lubricant was carefully cleaned from the side arm of the container which had been inserted into the ground joint, and the external surface of the whole vessel cleaned with alcohol, ether, and then wiped with a damp clean cloth.

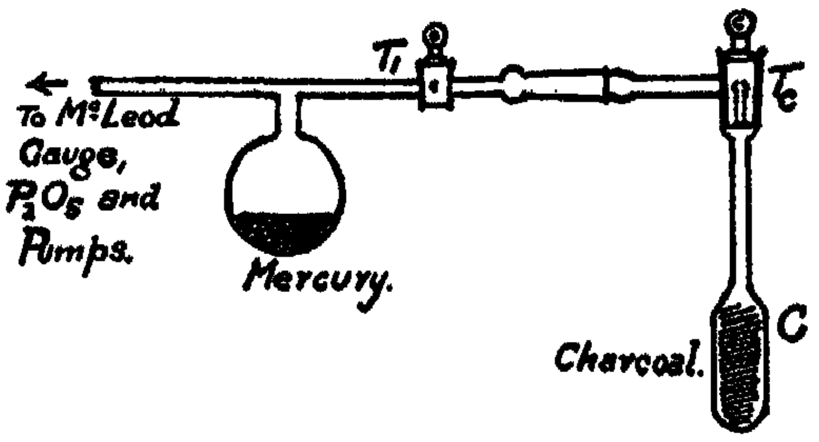

FIG. 1

Weighing was done against a glass counter-poise of same external volume and nearly same surface area. It received exactly the same treatment in cleaning with the exception of washing off the grease.

Weighings were correct to 0.00003 grams.

C was then re-attached to the apparatus, and the part between T_c and T_1 evacuated to 3 × 10^{-6} m.m.

This part of the apparatus was then shut off from the pumps and the tap T_c opened, and the charcoal left in contact with the mercury vapour for 13 hours. It was then detached and weighed.

A similar process was carried out with a further interval of 43 hours.

Table I shows the results obtained:—

TABLE I

Weight of charcoal, evacuated = 0.9508 grms.

Time	Increase in Weight
0 hours	0.00000 grms.
13 "	0.00011 "
56 "	0.00020 "

The above results confirm those of Coolidge so far as the order of magnitude is concerned, but are only about 1/250 of those obtained by Zelinsky and Rakusin whose experiments were carried out in such a way that air had access to the charcoal. It would therefore have contained about 1% of adsorbed air, partly nitrogen and partly oxygen. It was thought that possibly in their case there had occurred an oxidation of the adsorbed mercury vapour by the previously adsorbed oxygen.

The extremely low vapour pressure of the resulting mercuric oxide might account for the retention of an increase equal to 4% of the weight of the charcoal when it was exposed to an atmosphere free from mercury.

In order to test this hypothesis in such a way as to eliminate any uncertainty due to water vapour the following method was adopted.

After attaching the container C containing the same lot of charcoal to the ground joint the tap T_1 was opened through to the P_2O_5 tube and the air which had been at atmospheric pressure between T_0 and T_1 allowed to expand into the larger volume. The resulting pressure was about 8 m.m. This air was allowed to stand for 21 hours in contact with P_2O_5. T_0 was then opened and the charcoal exposed to this low pressure of dry air for 1½ hours. It was then evacuated in the cold to 3×10^5 m.m. and then removed and weighed.

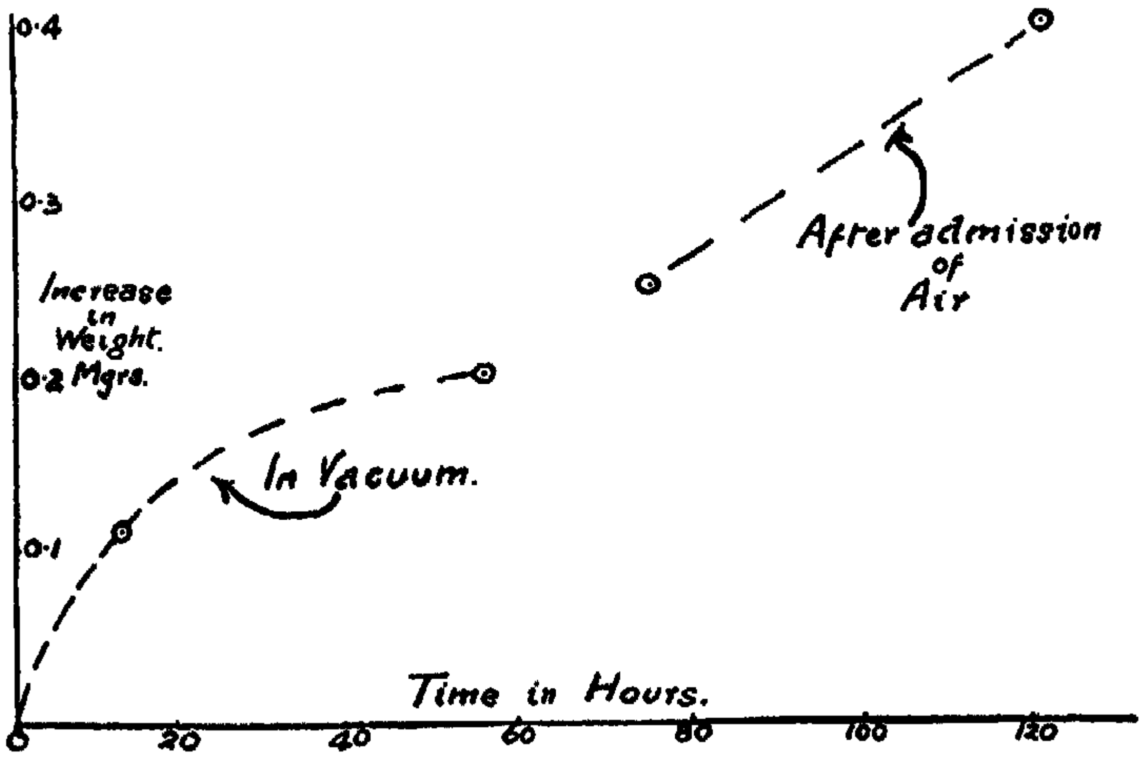

FIG. 2

It might have been more suitable for the purpose proposed to have the charcoal exposed to a constant pressure of dry air near atmospheric throughout, but the apparatus was not adapted for such a method. This would have given a greater quantity of adsorbed oxygen on the charcoal.

The container C was then re-attached to the apparatus, the part between T_0 and T_1 evacuated to 1.6×10^{-5} m.m., and then T_0 was opened; after standing 18½ hours at room temperature it was removed and weighed.

The same process was gone through again with a 46½ hours interval.

Time	Increase in Weight
0 hours	0.0000
18½ "	0.00005
65 "	0.00020

The above results are plotted in Fig. 2. Admittedly the results are hardly numerous enough to establish any oxidative influence, but they do show that any adsorption of mercury vapour by evacuated charcoal is very small. There appears to be a probability that there is some slight effect of oxidation.

It was decided to repeat the experiments of Zelinsky and Rakusin with the addition of blank experiments.

Samples of the same kind of charcoal were contained in weighing bottles having same volume in order to minimise the effect on their relative weights of any changes in temperature or pressure of the air contained therein.

The charcoal had stood for about 9 months in a glass stoppered bottle after being dried at 110°C.

The weighing bottles containing the charcoal were weighed against a counterpoise of same volume to within 1 cc. and nearly same weight.

One was placed with the counterpoise in a clean empty desiccator, the lid of the weighing bottle being placed beside it, that of the counterpoise being greased and placed in position thus ensuring that the air contained in it was constant in weight.

The other was placed in a similar desiccator in which was a shallow dish containing pure mercury which had been dried by running through filter paper. The lids of both desiccators were lubricated with Ramsay grease.

Previous to weighing the lids of the desiccators were removed, the lids placed in the weighing bottles which were then removed, and the desiccator lids replaced, the whole operation being carried out as quickly as possible.

Table II shows the increase in weight of the two weighing bottles and contents over a period of some days.

TABLE II

	No 2	No. 3
	Wt. Charcoal = 1.0459 grms.	1.0092 grms.
	Exposed to mercury vapour	Not exposed to mercury vapour
Date	Increase per gram of charcoal	Increase per gram of charcoal
26th Augt.	0.0000	0.0000
27th "	0.00488	0.00342
29th "	0.00523	0.00560
30th '	0.00649	0.00633
32st "	0.00209	0.00211
1st Sept.	0.00217	0.00215
2nd "	0.00301	0.00308
Total:	0.02387	0.02269

This gives an increase per gram of 0.00118 gm. (=0.12%) more in the case of the charcoal exposed to mercury vapour than in the case of that not so exposed.

The above experiment is open to the objection that the charcoals might be adsorbing vapours from the lubricant. A similar experiment was therefore carried out using desiccators whose lids were not lubricated. Two fresh samples of the same kind of charcoal were used.

TABLE III

Wt. charcoal =	1.00345	1.00210
Date	Increase in Weight	Increase in Weight
Sept. 3rd	0.0000	0.0000
" 14th	0.20650	0.21356
Mercury then placed in desiccator with No. 2		
Sept 14th to Octr. 13th	0.00925	0.01513

The excess of increase of weight of the charcoal No. 3 over that of the charcoal No. 2 was 0.00706 gms. for 11 day interval.

After exposing No. 2 to mercury vapour the excess of the increase of No. 3 over that of No. 2 was 0.00588 gms.

The difference may have been due to the fact that No. 2 was adsorbing mercury vapour or to the fact that both charcoals were coming more nearly to equilibrium with the water vapour in the air. Both causes might operate simultaneously. It is not possible to distinguish between them. It has been shown, however, that the method of Zelinsky and Rakusin is not reliable.

Summary

The adsorption of mercury vapour by activated charcoal has been determined at room temperature (12-14°C) in a vacuum.

The weight adsorbed is of the order of 0.2 mgr. per gram of charcoal.

Experiments were done to test the adsorption of mercury vapour by activated charcoal in presence of air. No definite indication of such adsorption was found.

Chemistry Department,
University of Melbourne,
Feb. 12, 1929.

PHOTO-VOLTAIC CELLS WITH SILVER-SILVER BROMIDE ELECTRODES. PART II*

BY S. E. SHEPPARD, W. VANSELOW, AND V. C. HALL

In Part I[1] of this series, the types of photo-cells used were described, and the general or typical photo-potential curve relating p. d. to time of exposure. This was found to consist of an initial very rapid negativization passing over into positivization.

Evidence was given that the positivization of the illuminated electrode with respect to the darkened electrode is due to bromine released from bromide ions attacking the silver. The action of bromine acceptors in delaying or suspending the positivization confirms this. On the other hand, the initial negativization was ascribed to the simultaneous release of electrons, some of which escaped combination with silver ions, but reached the silver electrode, thus increasing the electron pressure in the metal. To test this hypothesis, it was necessary to analyse more precisely the response of the cell within the first second of exposure to light.

A potentiometer and galvanometer system by virtue of its slow operation is inadequate for the study of this negative phenomenon because by the sudden deflection of the galvanometer at the beginning of the illumination period it merely indicates that there does exist a negative effect. The vacuum-tube voltmeter[1] was constructed to study the changes of the photo-potentials during the first minute of illumination. Through use of the apparatus it was soon evident that even a more rapid means of measurement than the low-period microammeter must be used in pursuing the investigation of this negativization process of the photovoltaic cell.

Records of the changes in the photo-potential differences between the two electrodes taking place during the first second of the illumination period were made by means of a General Electric oscillograph used in conjunction with a low-frequency amplifier. This system was employed in obtaining data herein presented.

Apparatus and Method of Procedure

The photo-voltaic cell[1] consisted of two silver—silver bromide electrodes immersed in an electrolyte. The cell was a large double U-tube having a quartz window for illumination of the electrode. The method of preparation of the electrodes has been described in detail in Part I. In short the electrode was a silver disk 10 mm. in diameter and approximately 2 mm. thick. A layer of silver bromide 0.0004 mm. thick was formed electrochemically on this silver disk. The nature of the photo-cell electrolyte will be described

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* Communication No. 362 from the Kodak Research Laboratories.

[1] Part I, published J. Phys. Chem., 33, 331 (1929).

in turn for the various experiments. One of the electrodes in the photo-cell was kept in darkness while the other one was exposed to the radiations of the quartz mercury vapor arc, which passed through a water cell with quartz windows. The layer of water was 10 mm. in thickness. In addition there was a 10 mm. layer of the photo-cell electrolyte through which the radiations had to traverse to reach the electrode. A 2-1/2 per cent copper chloride[3] solution was used as a filter for infra-red, having a transmission of about one per cent at 1.1 mμ. This solution was used in some experiments to ascertain the influence of the shorter infra-red radiations upon the negativization process. Inasmuch as whatever infra-red radiations reaching the electrode in absence of the copper chloride infra-red filter had apparently no influence upon the negative effect, this copper chloride solution was not used. The arc was 20 cm. distant from the electrode and operated with a fall of potential of 150 volts across its terminals. The two electrodes of the photo-cell were connected to the input terminals of a four-stage, low frequency amplifier leading to a General Electric oscillograph.

Amplifier-Oscillograph System

The circuit of a conventional four-stage resistance coupled amplifier is shown schematically in Fig. 1.

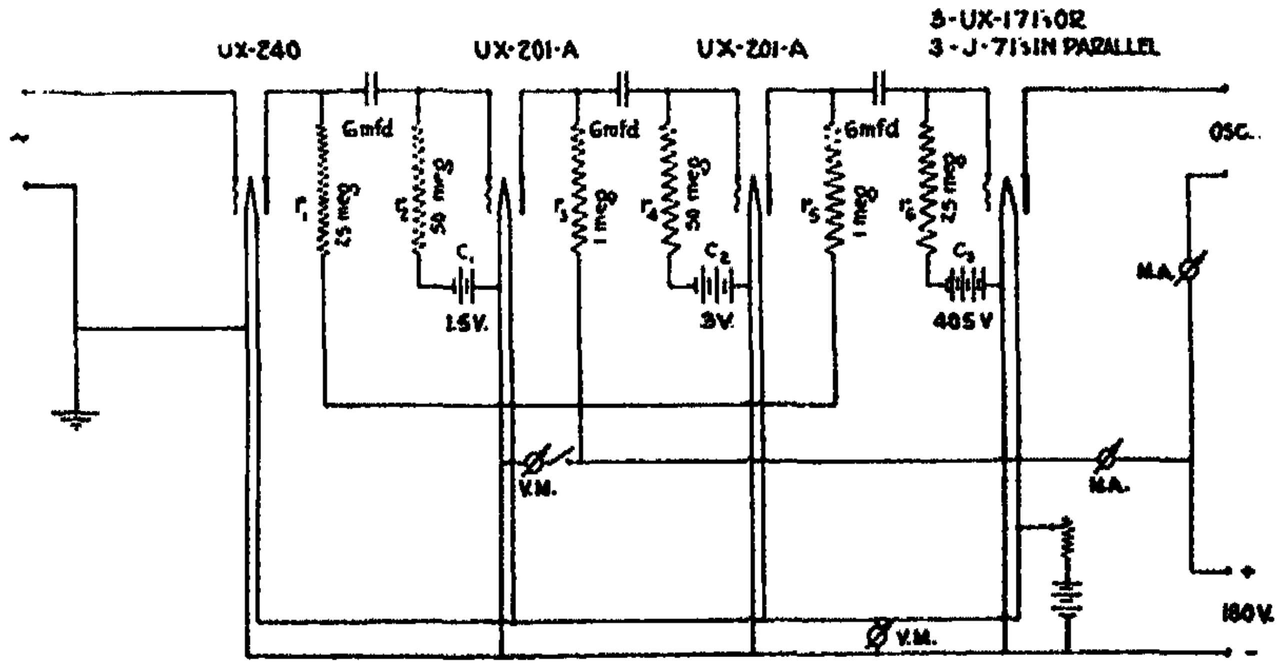

FIG. 1

The photo-voltaic cell whose resistance is approximately one-thousand ohms is connected across the grid and the negative filament of the first tube. Inasmuch as there exists a nearly zero difference of potential between the electrodes before illumination, there is no trouble due to changing grid bias on the first tube and the low input resistance tends to stabilize the amplifier. The various parts of the amplifier are clearly designated in Fig. 1.

Inasmuch as the amplifier was very sensitive to external electro-static disturbances, it was shielded by two cases, one of copper and the other iron.

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[3] Coblentz: Bull. Bur. Standards, 7, 657 (1911).

The leads from the photo-cell to the amplifier were rather long and were coated with a lead covering. This lead covering and the amplifier shields were grounded. At times when a high-resistant photo-cell electrolyte was employed a 60-cycle pick-up was evident in the oscillogram in spite of the shielding.

This amplifier was used in connection with a General Electric oscillograph. An S. V., high-sensitivity vibrator of the oscillograph was connected across the output terminals of the amplifier. An ordinary low-sensitivity vibrator of the oscillograph was connected to a 60-cycle current and thus employed as a timer.

The calibration of the amplifier-oscillograph by a potentiometer is shown in Fig. 2. The conditions of the amplifier circuit were as follows:—Four-stage amplification, with three Ceco J-71 tubes in the output. "C" voltage on power stage was 40.5; and "B" voltage was 180 on all tubes. Field current in the oscillograph was 0.35 ampere.

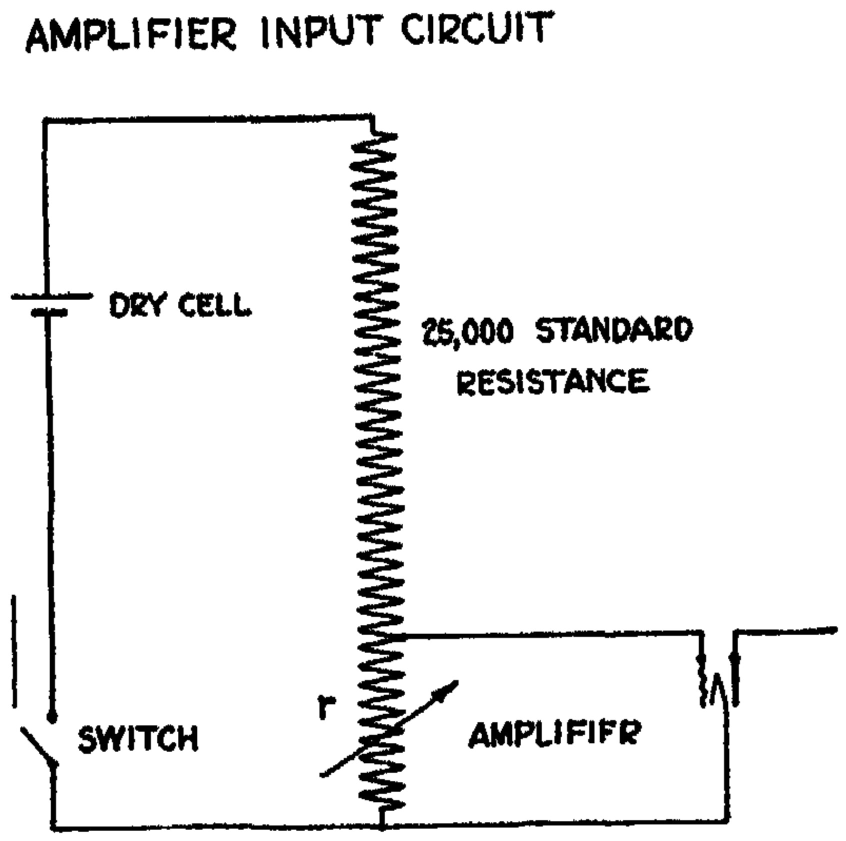

FIG. 2

The switch (S) was closed suddenly and left closed, thus applying a potential charge on the grid of the first tube. This travels through the amplifier as a surge similar to that caused by the illumination of the photo-cell. The curve thus obtained is that of the decay of charge through the amplifier and may be expressed as effective millivolts difference of potential at the input. The difference between this curve and that obtained experimentally by use of the photo-cell gives a measure of the amount of voltage caused by the photo-cell at any time. The drop in voltage in the photo-cell when illuminated is not usually so steep as in the case with the potentiometer; and further because the potential rises to zero faster than the calibration curve for the same millivolts input, the illuminated electrode does not remain at the maximum negative potential any great length of time.

Both the low and the high-sensitivity vibrators of the oscillograph were calibrated. The low-sensitivity vibrator was calibrated with its deflections away from the timer which is the 60-cycle curve at the bottom of the oscillo-

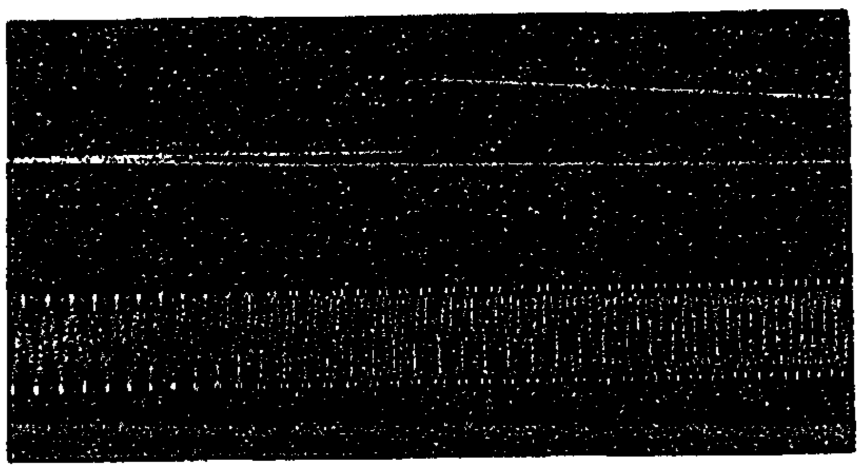

Fig. 3

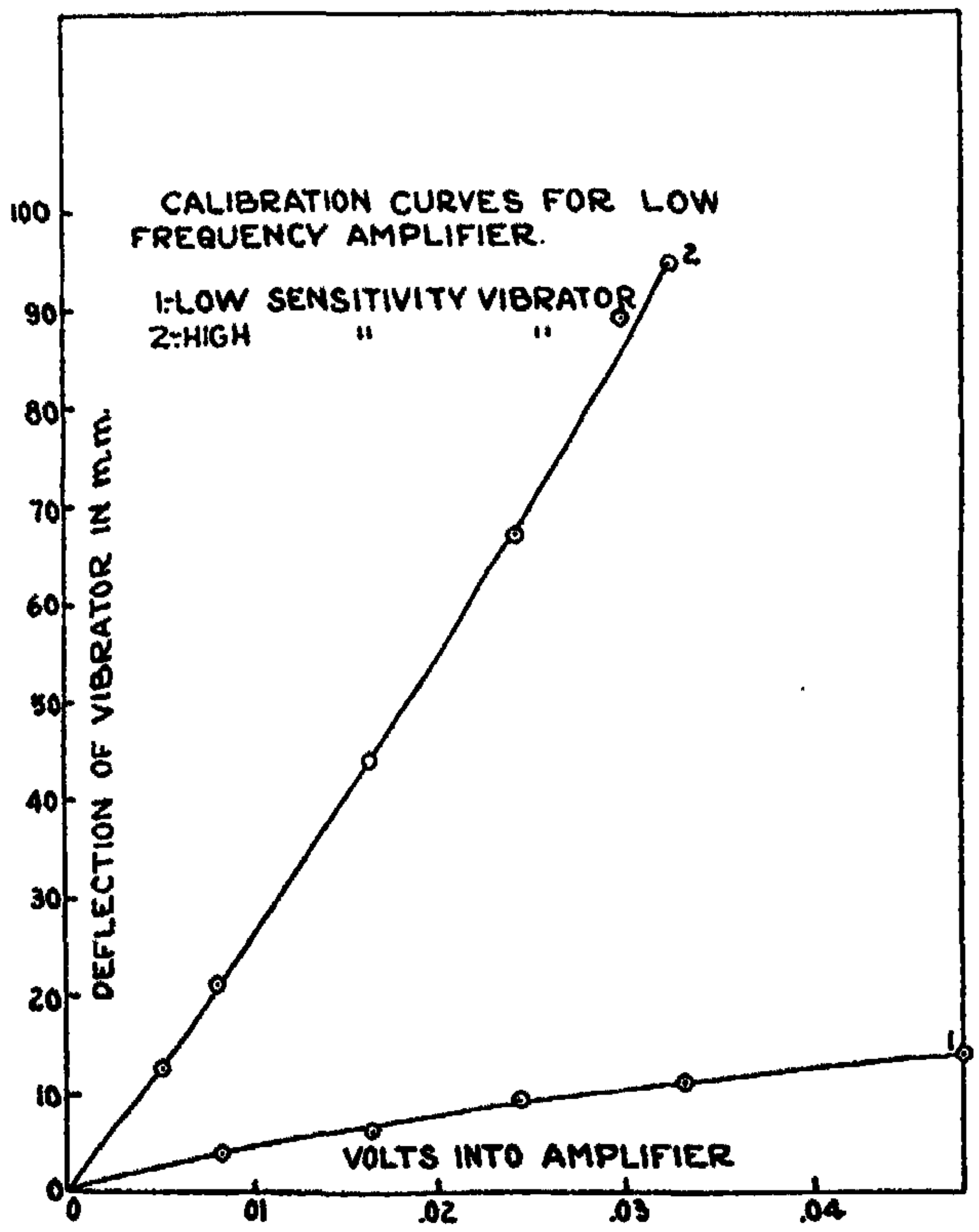

Fig. 4

gram while the high-sensitivity vibrator's calibration was conducted with its deflections towards the timer. The latter vibrator was used almost entirely for photo-potential measurements. After the oscillograms were made of a series of voltage settings of the potentiometer, the connections were changed over to the vacuum tube voltmeter[1] and the actual millivolts determined from the calibration data for the vacuum tube voltmeter. Fig. 3 shows the actual curve obtained with the low-sensitivity vibrator for an input of 33 millivolts. The 60-cycle time wave is shown at the bottom of the oscillogram. Fig. 4 shows the calibration curves of the low and high-sensitivity vibrators used in connection with the 4-stage amplifier.

Experimental

Investigations of various phases of the photo-voltaic phenomenon have been started using the amplifier-oscillograph. Among these are the following: Svensson-Becquerel effect, age of electrode, halogen acceptors, electrolytes, and intermittency of illumination.

Absence of Svensson-Becquerel Effect

The Svensson-Becquerel effect is the appearance of a photo-potential when the electrodes of a photo-cell are kept in darkness but the *electrolyte* is illuminated.[3,4] The important feature to bear in mind, of the experiments conducted by Lifschitz and Hooghaudt and by Svensson, is that when the platinum electrode, a non-reversible, polarizing electrode, is used the Svensson-Becquerel effect is observed; but if a reversible, unpolarizable electrode is used, no such effect is observed.

There arose the question in connection with this work when potassium bromide solutions were used for the photo-cell electrolyte whether or not any photo potentials were being created by the illumination of the electrolyte.

A few experiments were conducted using electrodes having a layer of silver bromide 0.0004 mm. in thickness immersed in electrolytes of the photo-cell. The following electrolytes were used: 1 —, 0.1 —, 0.00001 —, and 0.000001 normal potassium bromide soultions each having been saturated with respect to silver bromide. The electrolytes were kept in darkness but the electrolyte was illuminated using the emission spectrum of the quartz mercury vapor arc. Oscillograms of these experiments showed that there was *no Svensson-Becquerel effect influencing the results of this type of photo-voltaic cell.*

Age of Electrodes

The question arose as to what influence upon the photo-potentials the age of the electrodes had. Age may be interpreted here as being the time elapsing between the electrochemical formation of the silver bromide layer and the use of the electrodes in the photo-potential measurements. Several experiments were conducted in order to determine the magnitude of the differences if any. The results indicate that there are some small differences.

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[3] Svensson: Arkiv. Kemi., 7, 19 (1919); Diss. Upsala, Sweden.

[4] Lifschitz and Hooghaudt: Z. physik. Chem., 128, 87 (1927).

For each different age the results of a number of experiments were averaged. The thickness of the silver bromide layer on the electrodes was 0.0004 mm. The complete emission spectrum of the quartz mercury vapor arc was employed. The photo-cell electrolyte in these experiments in "aging" was in all cases a tenth normal potassium bromide saturated with respect to silver bromide.

Table I gives a summary of the experimental results of twenty-three experiments.

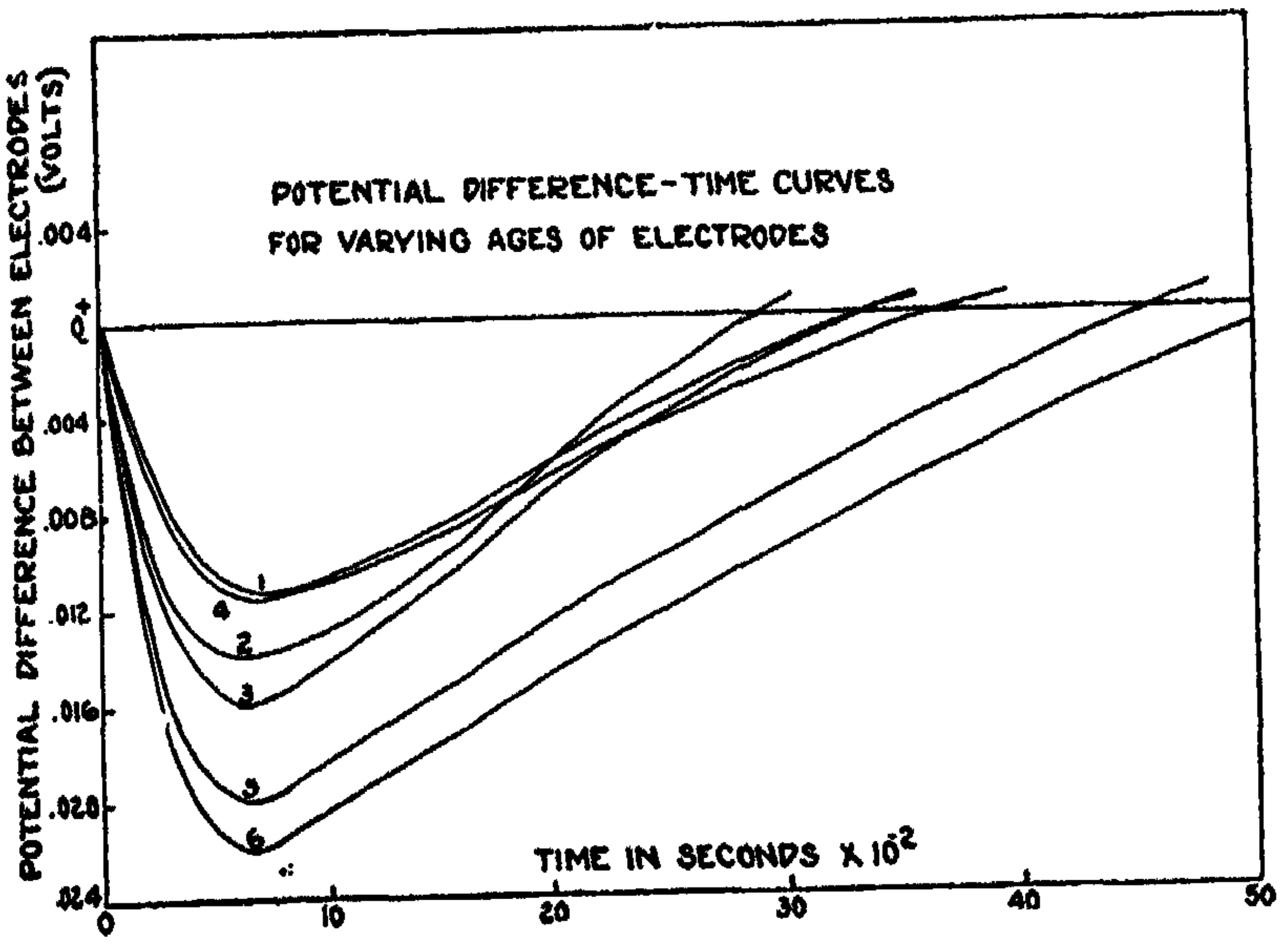

Fig. 5

Table I

Curve	I. Age of Electrodes	II. Maximum Difference of Potential (Initial Negative Drop) Volts	III. Time required to reach this Maximum Difference of Potential Seconds
1	2 minutes	0.0113	0.07
2	30 minutes	.0139	.055
3	4 hours	.0161	.062
4	24 hours	.0115	.06
5	7 days	.020	.064
6	8 days	.022	.064

Column II shows the maximum difference of potential or the drop in potential as the one electrode is illuminated and the other one kept dark. This value increases from the 2-minute to at least the 4-hour aging period.

It is possible that during that time some of the bromine which was formed during the electrochemical formation of the silver bromide is being removed by the medium in which the electrodes are standing during the "aging" time, or by diffusion to the silver electrode. It will be recalled[1] that it has been shown that bromine produces a positive photo-potential and if there should be no bromine present the negative photo-potential is not so much curtailed. However, it will be noticed at the 1-day age the negative photo-potential is not so great as at the 4-hour age. It is possible that there the silver bromide is in the process of changing its crystalline structure. At the age of seven or eight days the negative photo-potential has increased. The impurities, as hydrobromic acid and bromine, may have been fairly well washed out of the electrode and any crystalline transformation completed by this time.

Fig. 6

In all cases the time required for this negative photo-potential to reach its maximum value is approximately the same, *i.e.*, about 0.06 second, as is shown in Fig. 5.

Fig. 5 includes six potential difference—time curves which are each partially tabulated in Table I. Each curve represents an average of several oscillograms. Fig. 6 is a typical oscillogram.

Halogen Acceptance

If there is present in the photo-cell electrolyte, a substance absorbing bromine rapidly (*i.e.*, a halogen acceptor), this initial negative photo-potential is more pronounced and prolonged. Acetone semicarbazone is such an acceptor.

Fig. 7 shows two curves, comparing the averages of several oscillograms of the potential difference—time curves when acetone semicarbazone is present (2) in a 0.1 M concentration in the photo-cell electrolyte of 0.00001 normal potassium bromide solution saturated with respect to silver bromide, with the curve (1) when no acetone semicarbazone is present.

The time necessary for the negative photo-potential to reach a maximum value is greater with the halogen acceptor than without the acceptor. The negative effect is also more pronounced. The curves show that when the bromine is withheld by the halogen acceptor from the silver backing of the electrode, the negative photo-potential effect is prolonged.

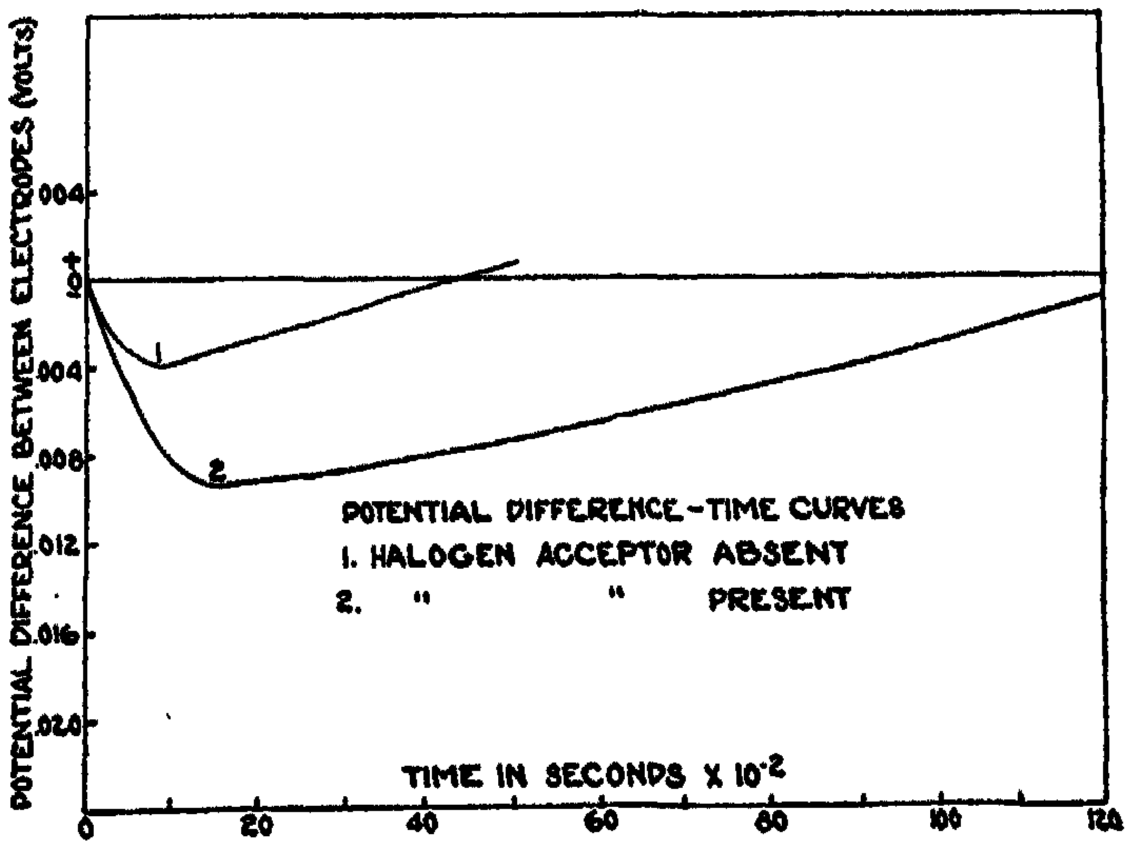

Fig. 7

Photo-cell Electrolytes

In another group of experiments the photo-cell electrolyte was changed, keeping the other controllable factors of the system constant. The silver bromide on the electrode was 0.0004 mm. thick. One electrode was exposed to the complete emission spectrum of the arc while the other electrode was kept in darkness.

The three electrolytes used, silver sulfate, silver nitrate, and potassium bromide, were each saturated with respect to silver bromide.

The averaged results of eighteen experiments are tabulated in Table II.

Table II

I. Photo-cell Electrolyte (Saturated with AgBr)	II. Maximum Difference of Potential (Initial Negative Drop) (Volts)	III. Time required to reach this Maximum Difference of Potential (Seconds)
0.1 N − KBr	0.0136	0.06
0.1 N − $AgNO_3$	.0265	.11
Ag_2SO_4 (water saturated)	.0247	.05

The maximum negative photo-potentials for the electrolytes of silver nitrate and silver sulfate are considerably greater than those for potassium bromide.

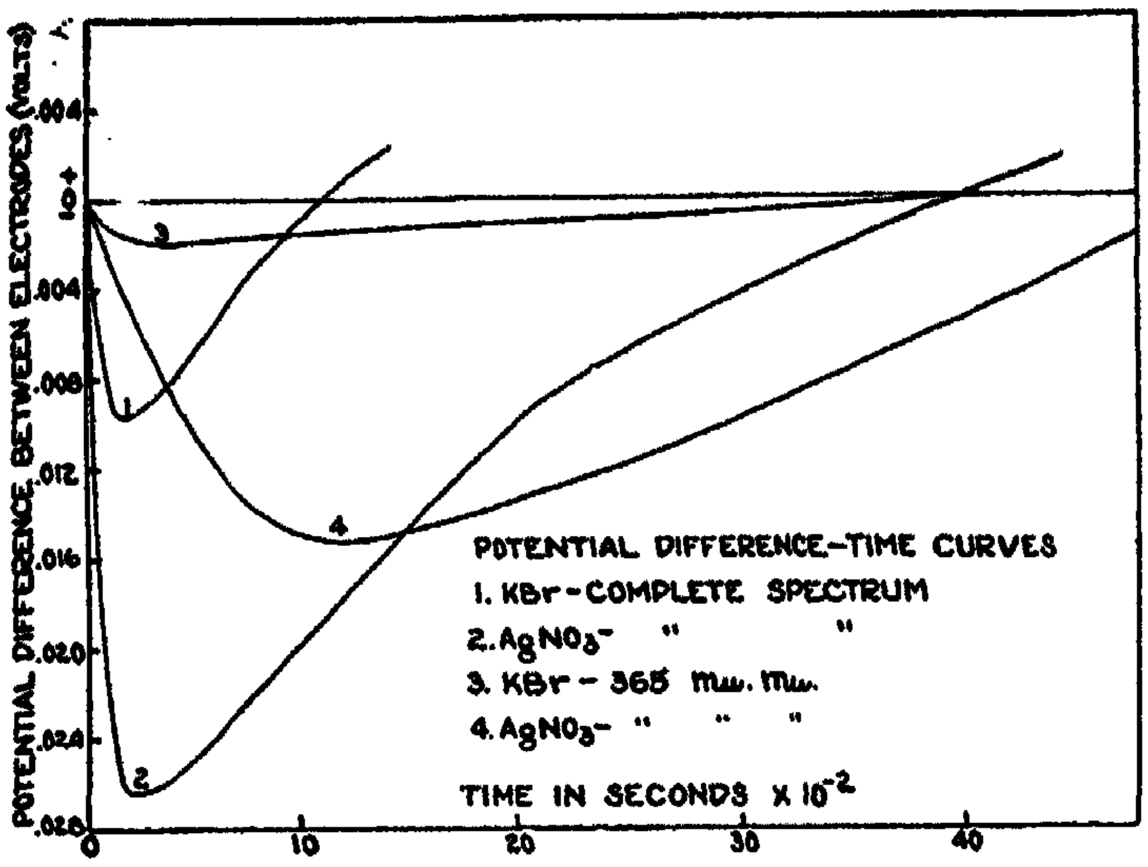

Fig. 8

In another series of experiments the following electrolytes were used: 0.02 normal solutions of potassium bromide, silver nitrate, silver sulfate, and silver acetate each saturated with respect to silver bromide.

TABLE III

Photo-cell Electrolyte (Saturated with AgBr)	Electrode illuminated by Radiation of Mercury Arc	Maximum Difference of Potential (Initial Negative Drop) (Volts)	Time required to reach this Maximum Difference of Potential (Seconds)
0.02 N – KBr	Complete Spectrum	0.0091	0.016
	365mμ	.0025	.066
.02 N – $AgNO_3$	Complete Spectrum	.0265	.022
	365mμ	.0140	.166
.02 N – Ag_2SO_4	Complete Spectrum	.0218	.022
	365mμ	.0122	.129
.02 N – $AgOOCCH_3$	Complete Spectrum	.0278	.013
	365mμ	.0149	.113

Fig. 8 contains four curves which are typical reproductions of oscillograms. When radiations of the complete emission spectrum of the mercury arc are used, the maximum negative photo-effect is attained more rapidly than when filtered radiation is employed. Compare curves 1 with 3 and 2 with 4 of Fig. 8. It will also be observed that the negative effect for the complete spectrum is not much more than twice that for the 365mμ line alone. This would indicate that the 365mμ line is as effective as all the remaining absorbed radiations together. This may not necessarily hold, especially for the reason that the individual effects may not be additive both with respect to intensity and speed. No data are available at present concerning antagonistic radiations for this particular system. Further investigations using monochromatic radiations and a still more sensitive indicator or recorder are now in progress.

The results for the three silver salts are pretty much the same. All of them are greater than that for potassium bromide. According to W. Frankenburger[5] when silver bromide is immersed under a solution of silver nitrate, its spectral sensitivity is increased to beyond 620mμ and possibly into the infra-red. On the other hand, if the silver bromide is under a solution of potassium bromide (acidified), the spectral sensitivity region is between 435 and 410mμ. The adsorption of ions on the outer surface of the silver bromide is responsible for its changing sensitivity.[6]

In the present case the spectral data are insufficient to establish the character of the sensitizing effect of silver ions for the negative photo-effect. But the fact that a great increase was shown with silver salts, as compared with potassium bromide at 365mμ, indicates that a large part of their effect here is due to halogen acceptance. Whether any extension of spectral sensitivity is shown will be brought out in later work on wave-length factors.

Intermittency

The study of intermittency of illumination is possible with this apparatus. The silver bromide layer in the electrode was 0.0004 mm. in thickness. The photo-cell electrolyte was 0.02 normal silver nitrate saturated with silver bromide. The complete emission spectrum of the mercury arc was used to illuminate the electrode. Intermittent exposures were caused by a sector wheel. Fig. 9 shows three curves for different frequencies of exposures. Curve 1 represents continuous illumination. For curves 2 and 3 the portions between E and D are periods of illumination while for portions between D and E both electrodes were in darkness.

Two conclusions appear possible from these observations. First, the intermittent exposure results, as indeed all the data with the oscillograph, demonstrate the inertialess character of the negativization phase. This is quite of the order obtained in the photo-conductance effect in crystals, and strongly supports the theory put forward in the first paper, that the negative effect is due to electrons set free by the process

$$\bar{Br} + h\nu \rightarrow Br + \Theta.$$

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[5] Z. physik. Chem., 105, 326 (1923).

[6] *Cf.* recent paper of Steiner: Z. physik. Chem., 125, 275 (1927).

The second conclusion appears to be that the total negative effect, expressed as the area under the curve below the zero axis, is somewhat lower for an interrupted exposure of low frequency of interruption than for a continuous exposure, but approaches the latter again as the frequency of interruption becomes greater.

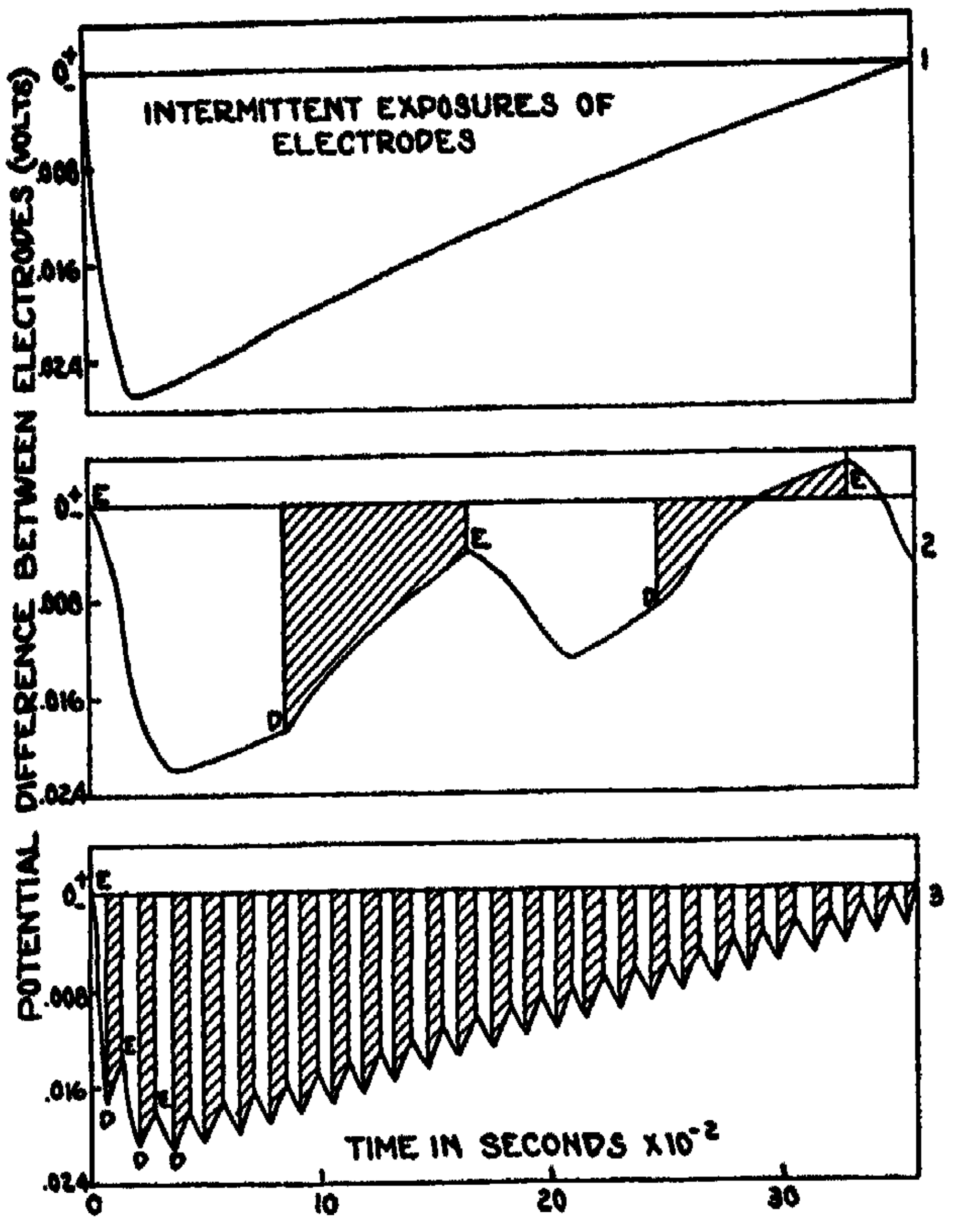

Fig. 9

In view of the fact that *two* processes of very different velocity, *viz.*, negativization by electrons, and positivization by halogen atoms or molecules, are occurring, a more intensive study of this phase is required before quantitative conclusions can be drawn.

Summary

A system comprising an amplifier-oscillograph is described whereby photographic records of photo-potential changes in the first second of illumination can be obtained. Photo-voltaic cells consisting of silver—silver bromide electrodes in various electrolytes have been studied with this arrangement, and the following factors studied:— age of electrode, Svensson-Becquerel effect, halogen acceptors, electrolytes, and intermittent exposure to light. The observations on the responses in the first second of exposure support the hypothesis proposed in the first paper. A more quantitative study of the initial response is planned.

Rochester, N. Y.,
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THE ACTIVATION OF HALOGENS AND CARBON MONOXIDE*

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The Activation of Halogens

If a mixture of hydrogen and chlorine be exposed to sunlight at ordinary temperatures, hydrochloric acid gas is formed;[1] combination also takes place when a piece of wood charcoal is introduced.[2] However, if the mixture be cooled to −12° and then exposed to bright sunlight it will stand for hours without a sign of combination.[3] Visible light causes the combination of hydrogen and bromine at 196° while the reaction is extremely slow in the dark at the same temperature.[4] There is nothing in the literature as to whether charcoal will do the same thing or not. It is shown later in this paper that charcoal does cause hydrogen and bromine to combine. Bancroft and Morton[5] in the Cornell laboratory have shown that hydrogen and iodine do not combine any more in the light from a 50-ampere arc than they do in the dark, even up to temperatures at which hydrogen begins to dissociate to an appreciable extent thermally (350°). This must mean that molecular hydrogen will not react with monatomic iodine in the concentrations present on exposure to the light used but that molecular hydrogen will react with monatomic bromine and with monatomic chlorine. This is true on the assumption that visible light does not activate the hydrogen appreciably. The validity of this assumption is supported by the fact that sunlight has no appreciable effect on the combination of hydrogen and oxygen to form either water[6] or hydrogen peroxide, while we know that monatomic hydrogen reacts with oxygen to form hydrogen peroxide.[7]

Charcoal evidently activates halogens but not hydrogen or oxygen to any appreciable extent. It is inert to a mixture of hydrogen and oxygen even at 100°,[8] although the gases are strongly adsorbed; when mixtures of air and hydrogen are passed over coal at 100°, no hydrogen is burned, while carbon monoxide and carbon dioxide are formed by the oxidation of the coal.[9] On the other hand, hydrogen and chlorine combine when a piece of charcoal is

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[1] Mellor: "Modern Inorganic Chemistry," 239 (1922).

[2] Mellor: "Inorganic and Theoretical Chemistry," 2, 159 (1922).

[3] Amato: Gazz., 14, 57 (1884); J. Chem. Soc., 46, 1237 (1884).

[4] Kastle and Beatty: Am. Chem. J., 20, 159 (1898).

[5] Proc. Nat. Acad. Sci., 15, 538 (1929).

[6] Mellor: "Modern Inorganic Chemistry," 102 (1922).

[7] Traube: Ber., 15, 2434 (1882).

[8] Taylor: Trans. Am. Electrochem. Soc., 36, 149 (1919).

[9] Tideswell and Wheeler: J. Chem. Soc., 115, 895 (1919).

introduced into a mixture of the two gases.[1] Melsens[2] made what he called chlorosulfuric acid (SO_2Cl_2) at room temperature by passing a mixture of sulfur dioxide and chlorine over ignited wood charcoal but could not make the bromosulfuric acid. Probably at temperatures high enough to make sulfur dioxide and bromine combine, the compound is not stable. This case is comparable to the inability of Berthelot to make carbonyl bromide from carbon monoxide and bromine photochemically; light decomposes the bromide.[3]

Damoiseau[4] used blood charcoal for halogenating aliphatic compounds. He could make anything from dichloroethane to hexachloroethane from ethyl chloride and chlorine, and could get any of the brominated derivatives of ethyl bromide and ethylene up to hexabromoethane.

Since halogens are activated by charcoal, it should be possible to make hydrobromic acid rapidly at a temperature lower than that employed for the photochemical combination by simply passing a mixture of the two gases over charcoal. A catalyst is invariably better than sunlight, as photochemical reactions are not very efficient.

The Catalytic Formation of Hydrobromic Acid

Hydrogen was bubbled through bromine contained in a vessel immersed in an ice bath and this mixture of hydrogen and bromine was then led over ignited wood charcoal at various temperatures. The effluent gases were bubbled through normal potassium iodide solution contained in two test tubes in series. The bromine left in the gaseous mixture reacts with the iodide to liberate iodine and the hydrobromic acid is absorbed directly in the solution as such. The iodine was titrated with thiosulfate and the residual solution was then titrated with alkali to determine the acidity due to hydrobromic acid. These values were calculated over to bromine and were compared with the loss in weight of the bromine container. The results checked within 2%.

The following table gives the results for three temperatures:

Temperature (°C.)	% of the bromine converted to hydrobromic acid
99°-100°	13.2%
150°-153°	49.1%
199°-201°	99.3%

A blank run made at 200° with no charcoal catalyst gave no hydrobromic acid at all.

From this it is evident that charcoal activates the bromine to such an extent that it will react with molecular hydrogen, the reaction proceeding rapidly and to an appreciable extent even at 100°.

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[1] Mellor: "Modern Inorganic Chemistry," 102 (1922).

[2] Compt. rend., **76**, 92 (1873); **83**, 145 (1876).

[3] Dyson: Chem. Reviews, **4**, 126 (1927).

[4] Compt. rend., **83**, 60 (1876); J. Chem. Soc., **30**, 617 (1876).

The Activation of Carbon Monoxide

It is well known that charcoal catalyzes the formation of phosgene from carbon monoxide and chlorine, and that this reaction also proceeds photochemically.[1] Moreover, it has been shown that if the temperature is kept down hydrogen does not interfere.[2] When a mixture of carbon monoxide and chlorine containing as high as 5% of hydrogen was passed over the highly activated charcoal used by the British army in respirators as much as 20 kilograms of phosgene were made at 14°-50° without diminished activity of the catalyst. Hydrogen and chlorine did not begin to combine until the temperature rose to 70°. Since chlorine is activated by charcoal in both cases and hydrogen scarcely at all, it must be that either carbon monoxide is also activated, or carbon monoxide is a better reducing agent than hydrogen, or both.

If carbon monoxide is activated, carbon monoxide and hydrogen should behave like bromine and hydrogen, and we would have a method for making formaldehyde or methanol without introducing the possibility of making methane, as catalysts which activate hydrogen do:[3]

$$\text{CO (activated)} + \text{H}_2 \text{ (molecular)} = \text{HCHO},$$

$$\text{CO (activated)} + 2\text{H}_2 \text{ (molecular)} = \text{CH}_3\text{OH},$$

but not $\text{CO} + 6\text{H (activated)} = \text{CH}_4 + \text{H}_2\text{O}.$

"Formaldehyde cannot be synthesized from a mixture of carbon monoxide and hydrogen by the action of sunlight, even in the presence of catalysts, although it is formed to some extent when the mixture is exposed to the ultraviolet rays from a quartz mercury lamp."[4] This means that molecular hydrogen (hydrogen is not activated by visible light) does not react with the carbon monoxide but that activated monatomic hydrogen does. Carbon monoxide is not necessarily activated by light of any kind and therefore the possibility of activated carbon monoxide reacting with molecular hydrogen is not ruled out.

In order to test out this idea, some experiments were made on mixtures of carbon, monoxide and hydrogen over various catalysts which might activate the former gas.

Experiments on Carbon Monoxide and Hydrogen

Carbon monoxide was prepared by dropping 85% formic acid into 85% phosphoric acid at 170°, according to the method described by Thompson.[5] The gas was led into a 12-liter gasometer, using water as the containing liquid.

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[1] Paternò: Gazz., 8, 233 (1878); John Davy: Phil. Trans., 144 (1812); Dyson: Chem. Reviews, 4, 109 (1927).

[2] Atkinson, Heycock and Pope: J. Chem. Soc., 117, 1410 (1920).

[3] In the methanol synthesis, using metal oxides as catalysts, it is necessary to run under pressure in order to prevent the formation of methane.

[4] Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 223 (1925); see also Berthelot and Gaudechon: Compt. rend., 150, 1690 (1910).

[5] Ind. Eng. Chem., 21, 389 (1929).

Hydrogen was run directly from a cylinder into the gasometer with the carbon monoxide. An approximately 1 : 1 mixture of the two gases were made. This mixture was used in all the runs except where otherwise specified.

Preliminary runs were made without drying the gases. The results were negative, however, so later runs were made with the gases dried by two calcium chloride, one soda-lime and one phosphorus pentoxide tubes in the order named. All the tubes were about one inch in diameter and nine inches long.

The charcoal used as catalyst was Nuchar No. 3—15 to 20 mesh—very kindly furnished us by the Industrial Chemical Sales Co., New York City. It was reactivated before use by pumping out for ½ hour at 400°.

The catalyst tube was about 20 mm. in diameter and one foot long. The latter half of the tube was filled with the charcoal, which was held in place with glass wool plugs. The first half of the tube was heated as well as the part containing the catalyst in order to preheat the incoming gases to the desired temperature.

The rate of flow of the gases through the catalyst was about 2-3 liters per hour. The effluent gases were bubbled through water and thence out the hood; near the end of a run, when all air had been removed from the catalyst tube, 200 cc. of the gas were collected for analysis for CO, H_2 and CH_4.

Qualitative tests were made on the water through which the gases had bubbled for formaldehyde and for methanol; the gas was analyzed by absorbing out the carbon monoxide with ammoniacal cuprous chloride and determining the hydrogen and methane in the residue by combustion with oxygen.

The results obtained follow:

Approx. CO : H_2 ratio in the mixture	t(°C.)	HCHO	CH_3OH	CH_4.	Gas used wet or dry
1 : 1	156°	none	none	0.26%	dry
1 : 1	199°	none	none	0.32%	dry
1 : 1	350°	none	none	0.35%	dry
1 : 1	410°	none	none	0.64%	dry
1 : 1	460°	none	none	1.34%	dry
1 : 1	500°	none	none	1.60%	dry

The above results seem to indicate that carbon monoxide is not activated by charcoal, even though the adsorption is very great. We get no formaldehyde or methanol but only methane and this not until the temperature rises to a point where hydrogen is activated thermally.

It may be that one of the products of the reaction is so strongly adsorbed as to poison the catalyst. With this in mind the gas velocity was stepped up to the highest possible rate obtainable with the apparatus. No variation in the results was noticed.

One run at 156° on a 2:1 carbon monoxide-oxygen mixture failed to yield any carbon dioxide with either a low or a high gas velocity (100 to 500 cc. per minute).

Carbon monoxide may be activated by hopcalite since this catalyst preferentially burns carbon monoxide from a dry carbon monoxide-hydrogen-air mixture at 0° even when the carbon monoxide content is as low as 0.2% in the mixture.[1] This was tested out by running a dry 1:1 mixture of carbon monoxide and hydrogen at 100° and 156° through a hopcalite kindly furnished us by Dr. Sebastian of the American Agricultural Chemical Company. In order to avoid oxidation of either carbon monoxide or hydrogen by air left in the catalyst tube, and consequent poisoning of the catalyst by moisture, the tube was evacuated cold, then brought up to the desired temperature with the pump still on, and finally the carbon monoxide-hydrogen mixture was passed through. Neither formaldehyde nor methanol was formed from three liters of gas and less than 1% of methane was produced. At 156°, some reduction of the catalyst occurred. In the light of these experiments is it probable that carbon monoxide is not activated enough by hopcalite to cause reaction with hydrogen.

The failure of either charcoal or hopcalite to activate carbon monoxide appreciably leaves us only with the assumption that carbon monoxide is a better reducing agent than hydrogen. This view has considerable support.

The following table of the temperatures at which various oxides are reduced by carbon monoxide and by hydrogen comes from data in Mellor:[2]

	Ag_2O_2	Ag_2O	HgO (yellow)	Hg_2O	CuO	HgO (red)	PbO_2	Pb_3O_4	PbO
CO	0°	0°	0°	0°	75°	90°	110°	150°	160°
H_2	0°	0°	50°	80°	125°	115°	150°	170°	190°

Further, carbon monoxide will readily reduce potassium chromate to chromic oxide and potassium carbonate, and neutral, acid, or alkaline solutions of permanganates.[3] Hydrogen does not reduce solutions of ferric chloride and of ferricyanide, concentrated nitric acid, chromic acid or aqua regia but will gradually reduce permanganate in neutral, acid or alkaline solutions at ordinary temperatures.[4]

Further still, carbon monoxide and chlorine unite at 14° over charcoal; hydrogen does not react from a carbon monoxide-hydrogen mixture until the temperature rises to 70°.[5] Moist carbon monoxide and air yield carbon dioxide at 90° or lower over hopcalite; hydrogen does not react from a hydrogen-carbon monoxide-air mixture containing as low as 0.5% carbon monoxide until 120°-125°.[6]

We may conclude therefore that carbon monoxide is a better reducing agent than hydrogen by a margin of about 30° to 50°.

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[1] Lamb, Bray and Frazer: Ind. Eng. Chem., **12,** 213 (1920).

[2] Mellor: "Inorganic and Theoretical Chemistry," **1,** 328-330 (1922); **5,** 942-943 (1924).

[3] Mellor: "Inorganic and Theoretical Chemistry," **5,** 942 (1924).

[4] Mellor: "Inorganic and Theoretical Chemistry," **1,** 328 (1922).

[5] Atkinson, Heycock and Pope: J. Chem. Soc., **117,** 1410 (1920).

[6] Lamb, Scalione and Edgar: J. Am. Chem. Soc., **44,** 2738 (1922).

Apparently another view is held for the case of hopcalite.[1] "Catalysts which actively promote the oxidation of carbon monoxide at 0°C. do not cause hydrogen and oxygen to combine below 70°C. This may be due to the anticatalytic effect of the water formed, since it has been shown that specially dried 'hopcalite' at 0°C. commences to burn hydrogen, but that the reaction soon stops." Water may be a poison in every case where hydrogen reacts with oxygen over a catalyst, but probably does not where hydrogen reduces an oxide. The presence of water vapor apparently does not affect the catalytic combustion of hydrogen over copper oxide.[2] At any rate carbon monoxide is a better reducing agent than hydrogen for substances in aqueous solution. The case of hopcalite must be a special one.

A further fact is also apparent from a consideration of the data on charcoal and on hopcalite given above. It has been shown that neither catalyst appreciably activates either carbon monoxide or hydrogen at the temperatures employed. We know that charcoal activates chlorine considerably. Therefore, hopcalite must activate oxygen considerably.

In order to check this assumption, some experiments were made on the oxidation of benzene vapor by atmospheric oxygen. Beilstein says nothing regarding the oxidation of benzene by oxygen in the absence of a catalyst. However, benzene can be boiled in the presence of air without any sign of decomposition taking place. If benzene is dropped into air at temperatures above 490° explosion takes place; there is no reaction at lower temperatures.[3] Our experiments were carried out by bubbling air through benzene at about 50° and passing the resultant benzene-air mixture through a tube packed with hopcalite maintained at a definite temperature. The first run was made with the catalyst at 210°. As soon as the mixture reached the catalyst the temperature rose rapidly to a maximum of 430°, the hopcalite reached a red heat, and the benzene was burned to carbon dioxide and water. A similar run made at 78° burned benzene completely to carbon dioxide and water. The catalyst in this case also became red hot and sintered down. There is therefore no doubt but that hopcalite activates oxygen to a considerable extent.

The inability of either hopcalite or charcoal to activate carbon monoxide led to a search for a catalyst that would cause activation. It is well known that iron and nickel form carbonyls with carbon monoxide and that these compounds dissociate reversibly on heating.[4] If we employ a temperature at which the carbonyl is, say, 50% dissociated, carbon monoxide will be continuously taken up and given off by the iron or nickel, and we have conditions ideal for the activation of carbon monoxide. At the instant at which a molecule of the carbonyl dissociates to the metal and carbon monoxide the latter must be at least momentarily activated and in a position to take up hydrogen.

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[1] Green: "Industrial Catalysis," 110 (1928).

[2] Pease and Taylor: J. Phys. Chem., **24**, 241 (1920).

[3] "International Critical Tables," **2**, 174 (1927); Jentzsch: Z. Ver. deut. Ing., **68**, 1150 (1924).

[4] Mellor: "Inorganic and Theoretical Chemistry," **5**, 953, 958 (1924).

A 3:1 mixture of hydrogen and carbon monoxide was passed over steel wool and over powdered iron reduced by hydrogen, at 156° and at 100°. At the former temperature, iron carbonyl ($Fe(CO)_5$) is about 50% dissociated. No formaldehyde or methanol was produced. This inactivity of iron may be due to the difficulty with which iron takes up carbon monoxide.[1] At the temperatures employed hydrogen is not activated by iron.

On the other hand nickel takes up carbon monoxide readily below 100°. Accordingly runs were made with a 3:1 hydrogen-carbon monoxide mixture over powdered nickel catalyst furnished by the duPont Co. at 78° (nickel carbonyl 1.1% dissociated[2]), 110° (about 12% dissociation), 180° and 230°. No formaldehyde or methanol was produced in any case even though at the two lower temperatures nickel carbonyl was formed. At the two higher temperatures, methane was formed, checking with the work of Sabatier,[3] and showing that the catalyst works.

Hence it must be concluded that molecular hydrogen does not react with activated carbon monoxide in the concentrations present. Carbon monoxide must deactivate itself faster than it will react with hydrogen.

On the other hand, it is relatively easy to cause either chlorine or oxygen to react with carbon monoxide. This is in accord with the fact that it is easier to decompose formaldehyde thermally to carbon monoxide and hydrogen than it is phosgene to carbon monoxide and chlorine.[4] The obvious difference is that hydrogen is essentially electropositive while chlorine and oxygen are essentially electronegative. Carbon monoxide must then be more electropositive in character than electronegative, and electronegative hydrogen should react most easily with carbon monoxide.

Sodium and potassium hydrides at the temperature at which reaction occurs give sodium formate and carbon; with carbon dioxide they give only sodium formate.[5] Calcium hydride on the other hand gives methane and hydrogen with both carbon monoxide and carbon dioxide.[6]

Calcium carbide is also formed when carbon monoxide is used. Nickel over 250° gives carbon and carbon dioxide along with the methane and water when a hydrogen-carbon monoxide mixture is passed over.[7] From this it appears that sodium, potassium and calcium at the temperatures at which reaction occurs catalyze the splitting of carbon monoxide into carbon and carbon dioxide more readily than the negative hydrogen can react with the carbon monoxide. The reactions cited above are all those of carbon dioxide, and not of carbon monoxide even when the latter is the reagent used.

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[1] Mellor: "Inorganic and Theoretical Chemistry," 5, 958 (1924).

[2] Mittasch: Z. physik. Chem., 40, 1 (1902).

[3] See Sabatier-Reid: "Catalysis in Organic Chemistry," 144 (1922).

[4] Hurd: "Pyrolysis of Carbon Compounds," 236, 569 (1929).

[5] Gmelin-Meyer: "Handbuch der anorganischen Chemie," 21, 164 (1925).

[6] Mayer and Altmayer: Ber., 41, 3074 (1908).

[7] Sabatier-Reid: "Catalysis in Organic Chemistry," 144 (1922).

The Mechanism of the Hydrogenation of Carbon Monoxide

Depending upon experimental conditions it is possible to obtain four kinds of reaction products from the hydrogenation of carbon monoxide, namely, methanol, a mixture of higher homologues of methanol called synthol, methane, and higher homologues of methane.[1] An almost 100% yield of methanol is obtained by passing a 1:2 mixture of carbon monoxide and hydrogen over suitable catalysts, usually mixtures of zinc oxide with promoters as copper oxide and chromic anhydride at 300°-350° and under 200 atmospheres pressure.[2] "From a consideration of the volumes entering in the reactions (between carbon monoxide and hydrogen to give formaldehyde or methanol or methane) it is apparent that the formation of methanol goes with the largest volume decrease—viz., from three to one, and hence would be most favored by increased pressure."[3] Synthol has been made by passing water gas (approximately 1:1 carbon monoxide and hydrogen) freed from sulfur compounds over iron and potassium carbonate at 400°-500° under 150 atmospheres pressure.[4] This synthol contains aliphatic acids up to C_8, aldehydes, ketones, alcohols up to C_9, with small amounts of hydrocarbons. The conditions for making synthol have been summarized:[5]

(1) For synthol formation the contact material must be a hydrogen-carrying metal plus an alkali; iron is the best metal (better than cobalt or nickel) and rubidium hydroxide or carbonate is the best alkali.

(2) The metal should be in chips and not powdered.

(3) Just enough—no more—alkali should be used to convert the iron to ferrite.

(4) For a given amount of contact mass there is an optimum gas velocity; the optimum temperature for iron is 410°, for nickel higher.

(5) Relative amounts of oily and watery products vary for the same material and experimental conditions; watery products vary most, especially as to alcohol and ketone content.

(6) Iron will retain full activity for a week but is gradually reduced to powder. Powdered iron favors carbon precipitation from the carbon monoxide but this is hindered by the alkali.

(7) Pressure variations from 70 to 150 atmospheres do not affect the yield.

(8) The richer in hydrogen the gas is the higher the yield of watery products but the oil boils lower and contains less hydrocarbons.

(9) Yields for a single passage over the catalyst are low; by circulation 27% of the heating value in the gas can be recovered in oil and alcohol formed.

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[1] Fischer and Tropsch: Ber., **59**, 832 (1926).

[2] Lewis and Frohlich: Ind. Eng. Chem., **20**, 285; Brown and Galloway: 960; Frohlich, Fenske, Taylor and Southwick: 1327 (1928).

[3] Lewis and Frohlich: Ind. Eng. Chem., **20**, 285 (1928).

[4] Fischer and Tropsch: Brennstoff-Chem., **4**, 276 (1923); Chem. Abs., **18**, 459 (1924).

[5] Fischer and Tropsch: Brennstoff-Chem., **5**, 201, 217 (1924); Chem. Abs., **18**, 3705 (1924).

(10) Mixtures of carbon dioxide and hydrogen can be used but they require a longer time than carbon monoxide and hydrogen. Methane with carbon monoxide or carbon dioxide will not yield synthol.

Yields of 100% methane are obtained by passing a 3:1 mixture of hydrogen and carbon monoxide over nickel at 230°-250° under atmospheric pressure, the reaction being $CO + 3H_2 = CH_4 + H_2O$.[1] If a sulfur-free water gas is passed over finely divided metals of the eighth group promoted with various metallic oxides or carbon at 270° under atmospheric pressure, higher homologues of methane from ethane up to solid paraffins are produced, the oxygen appearing not as organic oxygen compounds as in the high-pressure synthesis but almost wholly as carbon dioxide and water.[2] The process can be controlled to give almost any range of hydrocarbons desired. Practically no unsaturated hydrocarbons are formed. At higher temperatures, such as are used in the high-pressure synthesis, only methane is formed.[3]

Fischer and Tropsch have presented a theory for the formation of organic compounds containing oxygen as are produced in the making of synthol.[4] Their mechanism of the process will be reviewed here.

It must be assumed that in contact with a hydrogen-carrying metal, carbon monoxide and hydrogen add to form formaldehyde. In the presence of bases or salts of these bases with weak acids there are two possibilities: $2HC - O = CO_2 + CH_4$[5] or the reduction continues to methane and water. The water then reacts with carbon monoxide to give carbon dioxide and hydrogen. Both mechanisms lead to the same final state.

If the above-mentioned bases or salts are present we can imagine that the primarily formed formaldehyde reacts in other ways. Roelen[6] has shown that at ordinary pressures at 400°, two mols of formaldehyde in the presence of sodium carbonate give one mol of methanol and one mol of carbon monoxide. Paraformaldehyde in a hydrogen stream over pumice impregnated with potassium carbonate at 400° under 100 atmospheres pressure gives a considerable quantity of methanol.

We can consider, in the synthesis of butyl alcohol, for instance, that the formaldehyde can, under the given conditions, condense with simultaneous reduction to higher forms. In other words, we can say that it was made from a further synthesis from methanol.

In the same way as carbon monoxide unites with water to give formic acid, we can imagine methyl alcohol and carbon monoxide giving acetic acid. Genther[7] made sodium propionate from sodium ethylate at 190°; Ljubawin[8] made butyric acid from ethyl acetate by heating in a closed tube in the

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[1] Sabatier-Reid: "Catalysis in Organic Chemistry," 144 (1922).

[2] Fischer and Tropsch: Brennstoff-Chem., **7**, 97 (1926); Chem. Abs., **20**, 2065 (1926).

[3] Fischer and Tropsch: Ber., **59**, 923 (1926).

[4] Ber., **59**, 830, 832, 923 (1926); Brennstoff-Chem., **7**, 97, 299 (1926).

[5] Bone and Smith: J. Chem. Soc., **87**, 910 (1905).

[6] Unpublished work from the Kaiser-Wilhelm-Institut für Kohlenforschung.

[7] Ann., **202**, 290 (1880).

[8] J. Chem. Soc., **40**, 249 (1881).

presence of lime. It is noteworthy that carbon monoxide and alcohols give not the acids but alkyl formates. These are changed to the acids in contact with the alkaline catalyst.

If we assume that methanol gives acetic acid either directly or from methyl formate, it is easy to see how, through stepwise reduction of acetic acid, acetaldehyde and ethyl alcohol are formed in contact with the hydrogen-carrying catalyst. Likewise, acetone comes from catalytic decomposition of acetic acid in contact with the basic material of the catalyst; further, isopropyl alcohol can come through reduction of acetone.

By a mechanism as that outlined above, higher acids, alcohols, ketones and aldehydes can be formed, the limit of condensation (evidently seven or eight carbons in a chain) being limited by the pressure and temperature.

Another possible mechanism is the condensation of alcoholates with alcohols under pressure when heated for a long time to 200°-250°:[1]

$$C_mH_{2m+1}ONa + C_nH_{2n+1}OH = C_{m+n}H_{2(m+n)+1}OH + NaOH.$$

Methyl alcohol at 400°-430° in the presence of the alkali-iron catalyst, however, gave such a far-reaching decomposition to carbon monoxide and hydrogen that one must assume that higher boiling products come from the evolved gases with the aid of the contact material. It must be assumed, however, that the questionable reaction (that of Guerbet above) that at low pressures goes only in the absence of water may go in the presence of water under high pressures.

Still another possible mechanism is the dehydration of methanol to a CH_2 group which would polymerize to olefines which might hydrate to a higher alcohol. However, one must assume then that the aldehydes and acids come from a dehydrogenation or oxidation of the alcohol, whereas conditions are such (high hydrogen pressure) as to add hydrogen and not remove it. One would also expect the free CH_2 groups formed from dehydration of the methanol to combine to give hexylene and olefines. Actually these were not found in the reaction products.

For the low-pressure (ordinary pressure) synthesis of hydrocarbons from carbon monoxide, Fischer and Tropsch[2] have been forced to postulate another mechanism. The reactions take place over a hydrogen-activating catalyst as iron plus an oxide, zinc oxide or chromic oxide, which evidently act as promoters.

"A following-up of the reaction in a quantitative manner cleared up its mechanism. We observed that at first carbon from the carbon monoxide was taken up by the catalyst with carbide formation. This carbide was then decomposed by the hydrogen in the gas mixture in such a way that the metal was regenerated and the carbon was accordingly carried away as hydrocarbon. To all appearances it is a question not of a normal, carbon-poor carbide which is stable at high temperatures but of a carbon-rich car-

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[1] Guerbet: Ann. Chim. Phys., (7) **27**, 67 (1902); Bull., (3) **27**, 581 (1902).

[2] Ber., **59**, 830 (1926).

bide whose sphere of existence lies at a relatively lower temperature. There also resulted the fact that the carbon was dissolved out of the carbides by hydrogen not in the form of methane but in the form of higher homologues of the same. The correctness of our conclusion that under the conditions found by us the synthesis of hydrocarbons does not go by way of formaldehyde or methyl alcohol was especially supported by our determining that, in contrast to our observations on high-pressure catalysis, only hydrocarbons are ever formed and never organic compounds containing oxygen."

The theory is continued in the next paper by Fischer and Tropsch.[1] "If we worked under ordinary pressure with our catalysts at as high a temperature as was necessary with our high-pressure catalysis we obtained in place of homologues of methane exclusively methane itself."

"We must assume that the primary process of the formation of carbon-rich carbide is probably that at least one atom of carbon is held by each atom of divalent metal. Through the action of the hydrogen the carbon was carried over into a methylene group, that then polymerized according to the conditions and was then rapidly hydrogenated at a saturated hydrocarbon. Without this hydrogenation only saturated hydrocarbons that have a cyclic character can be formed by the polymerization of the methylene group. Small quantities of unsaturated hydrocarbons can be also deprived of hydrogenation. There appeared to us another essential fact regarding the process, namely, that the polymerization of the methylene group takes place faster than the hydrogenating action of the hydrogen on them does. If the latter were the faster, then the methylene groups would be carried over into methane. The hydrogenating action in the process must not be too strong, but on the other hand the catalytically active metal must have the ability to form a carbon-rich carbide. These are properties that from our earlier observations are found together especially in cobalt."

To summarize, the high-pressure synthesis passes through the formaldehyde and methanol stages and yields aliphatic compounds containing oxygen but very little hydrocarbons; the low-pressure synthesis does not pass through either formaldehyde or methanol but proceeds directly to hydrocarbons, the oxygen appearing as carbon dioxide and water.

On the other hand, formaldehyde hydrogenates readily over nickel to methanol,[2] but we find that methanol hydrogenates to methane over nickel at 230°, a temperature at which a mixture of carbon monoxide and hydrogen goes completely to methane. However, if the experiment is run with such poor contact with the catalyst that only 10% methane is formed from the theoretical mixture of carbon monoxide and hydrogen, then a hydrogenation of methanol gives as much carbon monoxide as methane. It appears therefore that the formation of methane from methanol takes place in two stages, first, a dehydrogenation to carbon monoxide and second, a hydrogenation

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[1] Ber., 59, 832 (1926).

[2] Sabatier-Reid: "Catalysis in Organic Chemistry," 159 (1922).

of this to methane and water. This is in accord with the theory of Fischer and Tropsch that low-pressure synthesis does not go through the formaldehyde or methanol stage.

Fischer's theory explains why we were unable to get any intermediate products from the hydrogenation of carbon monoxide. In addition, our work constitutes further support of this theory in that it was found impossible to make formaldehyde and methanol at ordinary pressures by using catalysts most likely to succeed from a theoretical standpoint.

Summary

1. Charcoal activates chlorine and bromine but does not activate either carbon monoxide, hydrogen, or oxygen to any appreciable extent. Hydrobromic acid has been made rapidly by passing a current of hydrogen containing bromine over charcoal. The conversion of bromine to hydrobromic acid is 13.2% at 100°, 49.1% at 150° and 99.3% at 200°.

2. In the phosgene synthesis over charcoal, chlorine is activated but the carbon monoxide is not, since neither formaldehyde nor methanol could be synthesized from carbon monoxide and hydrogen over charcoal, nor could carbon dioxide be made from carbon monoxide and oxygen over charcoal.

3. Hopcalite will not activate either carbon monoxide or hydrogen but does activate oxygen. No reaction between carbon monoxide and hydrogen could be observed but carbon monoxide, hydrogen and benzene are easily burned with air over hopcalite.

4. Hopcalite activates oxygen to such an extent that benzene vapor is completely burned to carbon dioxide and water at 78°, whereas benzene does not normally burn in air until the temperature is as high as 490°.

5. Evidence has been brought forward to show that carbon monoxide is a better reducing agent than hydrogen by a margin of about 30° to 50°.

6. Neither iron nor nickel will activate carbon monoxide to a point where a reaction between carbon monoxide and molecular hydrogen can be made to take place.

7. Carbon monoxide must be essentially electropositive in character since it reacts much more readily with oxygen and chlorine than it does with hydrogen, even when all three of the latter gases are activated. Carbon monoxide could not be made to react at all with molecular hydrogen; it will not react with electronegative hydrogen at a temperature lower than at least 500°, since calcium hydride at this temperature gives the same reaction produced by carbon dioxide; it reacts only with activated monatomic hydrogen.

8. The theory of Fischer and Tropsch as to the mechanism of the hydrogenation of carbon monoxide at high pressures and their theory as to the mechanism at ordinary pressures have been outlined. The latter theory explains why we were unable to get either formaldehyde or methanol since the hydrocarbons are formed by a direct hydrogenation of carbon as carbide.

9. Our work constitutes support of Fischer's theory in that it was found impossible to make formaldehyde or methanol at ordinary pressures even when catalysts theoretically most like to succeed were tried.

Acknowledgments

This research was suggested by Professor Wilder D. Bancroft and was carried out under his direction. The author welcomes this opportunity to thank him for his helpful and ever-ready criticism and aid.

The author also thanks The Industrial Chemical Sales Company, Inc. for furnishing the charcoal, Dr. Sebastian of the American Agricultural Chemical Company for the hopcalite, and the duPont Co. for the nickel catalyst used in this investigation.

Cornell University.

STUDIES ON GLASS

IV. Some Viscosity Data on Liquid Glucose and Glucose-Glycerol Solutions

BY GEORGE S. PARKS AND WALLACE A. GILKEY

Up to a few years ago a glass was generally regarded as a liquid of great viscosity. Recent studies, however, have demonstrated that in a number of properties, such as specific heat, coefficient of thermal expansion and dielectric constant, the glassy state more closely resembles the crystalline than the liquid state out of which it has been formed by cooling. Therefore, it is perhaps preferable to regard a glass as an amorphous solid rather than as an undercooled liquid. Nevertheless, the viscosity of a glass-forming liquid is of theoretical interest and in some cases, those of commercial inorganic glasses for instance, may also prove of great practical importance.

In the present investigation, which is essentially an outgrowth of previous studies[1] on organic glasses, we have measured the viscosity of liquid glucose over a temperature range of almost 80°. In this connection we have also studied the viscosity of a series of glucose-glycerol solutions, all of which liquids, when properly cooled, form clear, reasonably stable organic glasses.

Method and Apparatus

The method employed was by no means new in principle, its essential features having been used in the past by numerous workers.[2] The liquid which was to be studied was placed in a stationary, cylindrical container and a second cylinder, smaller and co-axial with this, was next introduced to a certain depth of immersion. The inner cylinder was then caused to rotate under the influence of a given torque and the rate of rotation was measured. From the dimensions of the apparatus the viscosity of the liquid could then be calculated.

Two different instruments, based upon this method, were used in the course of the measurements. For viscosities in excess of 10^6 poises we constructed our own viscometer. The outer cylinder, containing the liquid, consisted of a stout Pyrex test-tube (2.2 cm. internal diameter) which was tightly clamped to an iron stand and was thus held stationary. A long steel or glass rod (about 0.7 cm. in diameter) served as the inner, rotating cylinder. This rod rotated in a bearing which held it in a central, vertical position in the test-tube and maintained a constant depth of immersion (about 7.5 cm.) in the liquid under investigation. Above the bearing the rod was bent outward at a right angle for a distance of 15 cm., and a brass weight, operating upon the

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[1] Parks and Huffman: J. Phys. Chem., **31**, 1842 (1927); Parks, Huffman and Cattoir: **32**, 1366 (1928); Cattoir and Parks: **33**, 879 (1929).

[2] Couette: Ann. Chim. Phys., (6) **21**, 433 (1890); Searle: Proc. Camb. Phil. Soc., **16**, 7 (1912). See also Hatschek: "The Viscosity of Liquids," 50 (1928).

free end thru a pulley, thereby provided a suitable moment of force for rotating the inner cylinder of the viscometer. A needle pointer, attached to this lever arm and moving along a millimeter scale, served to determine the amount of rotation, the corresponding time, when brief, being measured by a stop-watch and, when longer, by a good ordinary timepiece. The test-tube and contents were placed in a Dewar jar, which served as a small adjustable thermostat. For measurements below 0°C. the bath liquid was ethyl alcohol cooled with carbon dioxide snow or liquid air, and the temperatures were measured with a copper-constantan thermocouple, accurate to within 0.3°C. Above 0°C. water was the bath liquid in the Dewar jar and temperatures were determined to 0.1° with a mercury thermometer.

For such an apparatus, if the viscous effects due to the liquid between the co-axial cylindrical surfaces be given sole consideration, the viscosity can be calculated by the formula,

$$\eta = \frac{C\,(R_2^2 - R_1^2)}{2\,\omega\,AR_1\,R_2^2} \qquad (1),$$

where C is the torque or moment of force[1] producing rotation of the movable rod, ω is its resulting angular velocity, A and R_1 are, respectively, its lateral area and radius, and R_2 is the inside radius of the Pyrex tube. From a theoretical standpoint the viscous effect on the lower end of the moving rod should have been taken into consideration also. However, this quantity could not be exactly calculated; and we therefore neglected it, since owing to the dimensions of our apparatus it was undoubtedly very small. Experimentally we were fully justified in such a procedure, because the substitution of a rod of double the diameter and the use of various depths of immersion, etc. gave fairly concordant results as calculated by equation 1.

For viscosities smaller than 10^6 poises we employed a Stormer viscometer which we modified slightly because it has been originally designed for use with less viscous liquids. In this instrument the brass inner cylinder was 2.46 cm. in diameter and was immersed to a depth of 2.11 cm. The outer cylinder was a brass cup 4.85 cm. in diameter, which contained about 60 cc. of the liquid under investigation. In this case the inner, co-axial cylinder was also the one which rotated but the rate of rotation was always small enough to avoid appreciable centrifugal effects. For temperature control the brass cup and contents were immersed in a paraffin bath which could be heated by a small gas burner. The entire viscometer outfit was then placed in a small closet, provided with a glass window. This closet served as an adjustable air thermostat, the temperature of which could be varied over the range from 40° to 170°C. The temperatures of the liquid under investigation were determined immediately after each viscosity measurement by a mercury ther-

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[1] A certain small torque was found necessary to overcome the friction in the bearings and pulleys of the apparatus when no liquid was present in the Pyrex tube. Hence, when a liquid was being studied, this value was always subtracted from the total torque employed; C then represents the net torque required to overcome the viscosity of the liquid.

mometer. The times for ten rotations were measured by a stop-watch. With this Stormer viscometer the viscosities were calculated by the equation,

$$\eta = \frac{C\,(R_2^2 - R_1^2)}{2\,\omega\,(A + B)\,R_1R_2^2} \qquad (2),$$

where A, as before, is the lateral area of the inner cylinder and B represents approximately the correction for the end effect.

The viscosity results obtained by the use of these two instruments, while not of extreme precision, were undoubtedly as accurate as the reproducibility of the glucose samples warranted.

Preparation of the Liquids

As in the earlier studies, the samples of liquid glucose were prepared by heating crystalline α-glucose (Pfanstiehl Chemical Company) in a flask immersed in a paraffin bath. The glucose crystals melted at about 146° C and were then maintained under a vacuum at a somewhat higher temperature for a short time, usually about five minutes, in order to eliminate bubbles of air or water vapor. When the liquid had become fairly clear, air was admitted and the sample was allowed to cool; it was usually straw-colored. Considerably longer periods of heating at 165° or above led to noticeable decomposition and a product which was dark brown in color.

The glycerol employed in some of the early work was a C. P. "Pfanstiehl" product, which had a density corresponding to a water content of about 3%. Hereafter in this paper it will be referred to as "97% glycerol." In our final work some of this material was subjected to distillation under a pressure of 5 to 10 mm. Rejecting the first and last quarters, we employed the middle portion in the present research. It had a specific gravity corresponding to 99.9% glycerol on the basis of the recent data of Bosart and Snoddy.[1] The various two-component liquids containing glycerol and glucose were prepared by mixing the proper amounts of the two components and then heating until complete solution had taken place. The resulting liquids were either colorless or a light straw-color.

Experimental Results

Very early in the course of the present investigation the question arose as to whether we were dealing with true viscosity or with plasticity as the temperatures approached the region of the glassy state. With a case of true viscosity the velocity gradient, dv/dx, between a unit plane surface moving parallel to a stationary plane is directly proportional to the shearing force, F, as shown in the following equation:

$$dv/dx = \Phi F \qquad (3),$$

where Φ is the fluidity, the reciprocal of the viscosity. On the other hand, the corresponding equation[2] for a plastic material is

$$dv/dx = \mu(F - f) \qquad (4),$$

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[1] Bosart and Snoddy: Ind. Eng. Chem., 19, 509 (1927).

[2] Bingham: J. Phys. Chem., 29, 1203 (1925).

where μ is the "mobility" and f is the "yield-value." For viscometers such as ours, if velocities of shear be plotted as ordinates against the corresponding shearing forces as abscissas, the resulting curve is a straight line passing thru the origin in any case of true viscosity, while in a case of plasticity the straight line should cut the X-axis at some distance to the right of the origin. Thus the distinction between the two phenomena can be readily made.

To answer this question the rate of rotation of the rod in our first viscometer was determined for a series of different torques in the case of liquid glucose at 44°C. and also in the case of a solution consisting of 82% glucose and 18% glycerol at the respective temperatures, 20°, 16°, 12°, 8°, 4°, 0°, and −4°C. The data thus obtained for the glucose-glycerol solution at 12.0° are given in Table I and are represented graphically in Fig. 1. They are typical of the other data as well. In all cases the results indicated that we were dealing with true viscosity and not with plasticity.

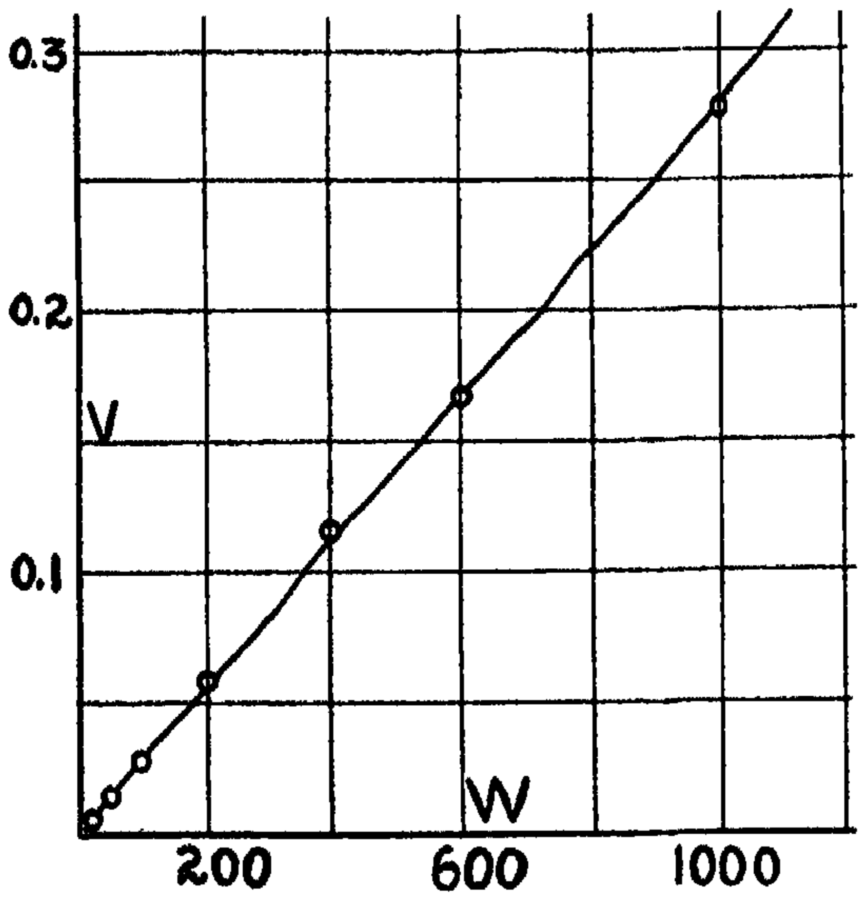

FIG. 1
Velocity of viscometer pointer, V, plotted against W, the weight used for producing rotation.

Viscosity Data for Liquid Glucose.—Using the first viscometer, which by its dimensions was specially adapted for the measurement of very high viscosities, we next determined the viscosity-temperature curve between about 60° and 30°C. for five different samples of liquid glucose. The essential data are given in Table II and are represented graphically in Fig. 2. All these five curves are very similar in character, altho they do not coincide. Thus the temperatures at which the viscosity is 10^{10} poises are, respectively, 36.1°, 33.6°, 34.9°, 34.6°, and 31.4°C. Evidently no two samples of the liquid glucose were exactly alike. This situation may be due in part to two different

TABLE I

Viscosity Test made at 12.0°C. upon a Two-Component Liquid containing 82% (by weight) Glucose and 18% Glycerol

Velocity of viscometer pointer in cm. per sec. V	Weight used to produce rotation, in grams W	Ratio: V/W
0.0051	20	0.00025
0.0141	50	0.000282
0.0282	100	0.000282
0.0582	200	0.000291
0.1155	400	0.000289
0.1667	600	0.000278
0.277	1000	0.000277

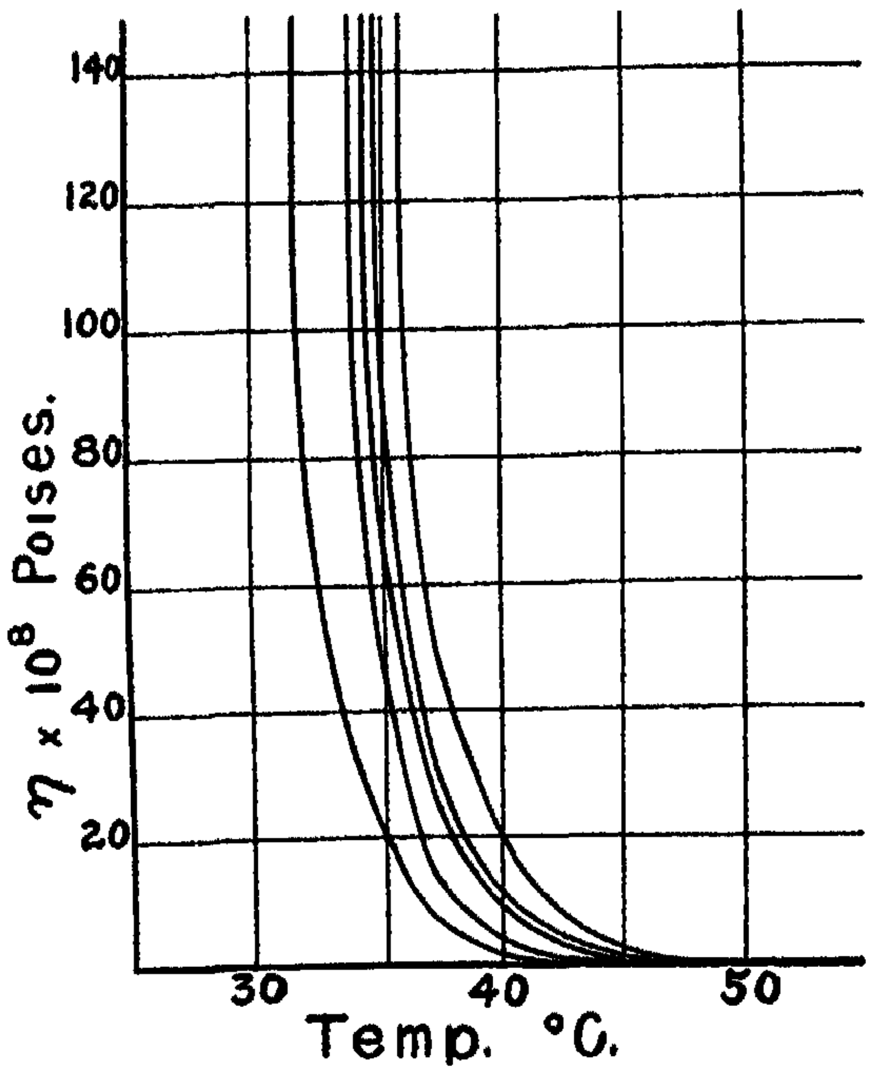

FIG. 2

Viscosity curves for five different samples of liquid glucose as the hardening temperature is approached

factors: viz., (1) differences in the character of the glucose in the various samples, as evidenced by different degrees of mutarotation, and (2) the presence of varying amounts of impurities incurred in the preparation of the liquids.

Polarimetric measurements were made on aqueous solutions of the glucose used in preparing the samples. The results indicated that the crystalline material was about 95% α and 5% β-glucose. On the other hand, six different samples of liquid glucose gave specific rotations varying from +42° to +49°; and their rotary powers showed practically no change with temperature as the samples were cooled over a range of 100°C. and the glassy state was attained. Similarly the various liquids in the glucose-97% glycerol system showed specific rotations ranging from +48° to +58°. As the specific rotations of aqueous solutions of pure α and pure β-glucose were found by Hudson and Yanovsky[1] to be +113.4° and +19°, respectively, we are justified in concluding that our several liquids contained varying proportions of the α and β forms, with the latter predominating in all instances. Differences in the temperature and in the duration of heating incident to the preparation of the various samples may have produced, therefore, these appreciable differences in the relative quantities of the two forms and likewise somewhat different viscosity curves.

TABLE II

Viscosity Data for Five Samples of Liquid Glucose below 60°C

Temp. °C.			Viscosity, η, in poises		
	I	II	III	IV	V
28.0	—	—	—	—	1.13 (10^{11})
29.0	—	1.37 (10^{11})	—	—	—
30.0	—	6.83 (10^{10})	—	—	3.57 (10^{10})
32.0	1.30 (10^{11})	1.79 "	3.90 (10^{10})	3.69 (10^{10})	8.08 10^{9})
34.0	3.63 (10^{10})	1.08 "	1.95 "	1.42 "	3.01 "
36.0	1.05 "	3.16 (10^{9})	5.30 (10^{9})	7.41 (10^{9})	1.21 "
38.0	4.10 (10^{9})	9.78 (10^{8})	2.44 "	2.05 "	4.70 10^{8})
40.0	2.12 "	3.84 "	1.12 "	9.20 (10^{8})	2.06 "
44.0	3.63 (10^{8})	7.17 (10^{7})	2.09 (10^{8})	1.65 "	4.52 (10^{7})
48.0	7.50 (10^{7})	1.68 "	3.26 (10^{7})	2.83 (10^{7})	9.70 (10^{6})
52.0	1.66 "	—	8.35 (10^{6})	7.84 (10^{6})	2.62 "
56.0	—	—	2.24 "	2.63 "	6.2 (10^{5})

Earlier observations on the effect of heating liquid glucose for considerable periods at 165°C. or above had indicated to us that more or less chemical change took place. There was a noticeable darkening of the color of the sample, and water appeared to be formed and evolved as vapor. Accordingly, in the present investigation we measured the viscosities, as the liquid was cooled to a glass, of a glucose sample which had been prepared in the usual way and then redetermined the viscosities after heating the liquid at 165°-170°C. for twenty minutes This heating procedure was repeated twice. The four viscosity-temperature curves thus obtained were similar; but in each case, after reheating, the curve was shifted about 4° along the temperature axis in the direction of the origin. A similar shift toward lower temperatures, this time of about 8° in magnitude, was observed when 1% of water was dissolved in another liquid glucose sample. It was found that both these experiments

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[1] Hudson and Yanovsky: J. Am. Chem. Soc., 39, 1035 (1917).

were reproducible. Thus it may well be that the prolonged heating at 165° decomposed the sugar and produced water at a faster rate than it was evolved; the observed shift in the viscosity curves can then be accounted for by an increase of 0.5% in the water content of the liquid glucose for each twenty-minute heating period. While the time of heating in preparing the five different samples of Fig. 2 was never over four or five minutes, it is quite possible that part of the observed differences are due to a small amount of decomposition[1] in some cases with a resulting increase in the water content.

None of the measured viscosities go above 10^{11} poises and no measurements on pure liquid glucose were made below 28°C. However, extrapolations can easily be carried beyond these values, since the curve obtained by plotting the logarithms of the viscosities against the corresponding temperatures is regular and, over a short temperature interval, does not deviate greatly from a straight line. Using the data of sample III as fairly representative of liquid glucose, we have found by this means a viscosity value of $10^{13.0}$ poises at 25°C. This is the middle point in the temperature interval, 20°-30°C., within which a sharp 200% increase in the coefficient of thermal expansion takes place and the values for the refractive index[2] and dielectric constant[3] begin to change rapidly. For purposes of brevity it may well be termed the *hardening point* of liquid glucose or the *softening point* of the glass. While its location at 25°C. and a viscosity of $10^{13.0}$ poises is admittedly very arbitrary, the fact that the temperature of this viscosity value is reproducible to within ±2° in the case of five samples, coupled with the fact that the other properties just mentioned show marked changes around this point, justifies in a sense the adoption of some such temperature as a crude division mark between the liquid and glassy states. Tammann and Hesse[4] in a very interesting paper have recently come to essentially the same conclusion with respect to the hardening point, and others who have studied the viscosities of glass-forming liquids have roughly checked this value of 10^{13} poises. Thus Samsoen[5] states that the sharp change in the coefficient of thermal expansion of several amorphous substances comes at a viscosity of 10^{14}. Likewise in the case of a number of silicate glasses English[6] has obtained a viscosity value of approximately $10^{12.8}$ for the "annealing temperature," while Stott[7] suggests "that the change occurring in the constitution of glass should happen when the viscosity is in the neighborhood of $10^{13.7}$ poises." In this connection, however, it should be noted that for both propylene glycol and glucose the sharp

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[1] Further evidence of the decomposition of liquid glucose in this way was obtained by heating a sample weighing 26.16 gm. for over ninety minutes under a vacuum at 170°C. The material lost about 4% of its initial weight during the process. While the heat treatment of the liquid in this test was undoubtedly more severe than that incidental to the preparation of the other samples, the result again indicates the possible existence of some decomposition products in the several liquids employed in the viscosity determinations.

[2] Parks, Huffman and Cattoir: J. Phys. Chem., **32**, 1374 (1928).

[3] Cattoir and Parks: J. Phys. Chem., **33**, 882 (1929).

[4] Tammann and Hesse: Z. anorg. allgem. Chem., **156**, 256 (1926).

[5] Samsoen: Compt. rend., **182**, 517 (1926).

[6] Society of Glass Technology: "The Constitution of Glass," 72 (1927).

[7] Society of Technology: "The Constitution of Glass," 75 (1927).

rise in the heat capacity curve is completed at a temperature somewhat below the "softening point," as here defined. While this situation is rather surprising, we are inclined to regard it as real, altho it might be explained away by the statement that the various kinds of measurements were never made upon precisely the same sample of material.

With the modified Stormer viscometer measurements were made upon a sample of liquid glucose over the temperature range from 60° to 110°C. At about 105° the liquid began to show signs of devitrification and above 110° this tendency toward crystallization became so pronounced as to prevent further measurements. The viscosity data are given in Table III. In Fig. 3 we have plotted the logarithms of the viscosities against the corresponding temperatures and for purposes of completeness we have also

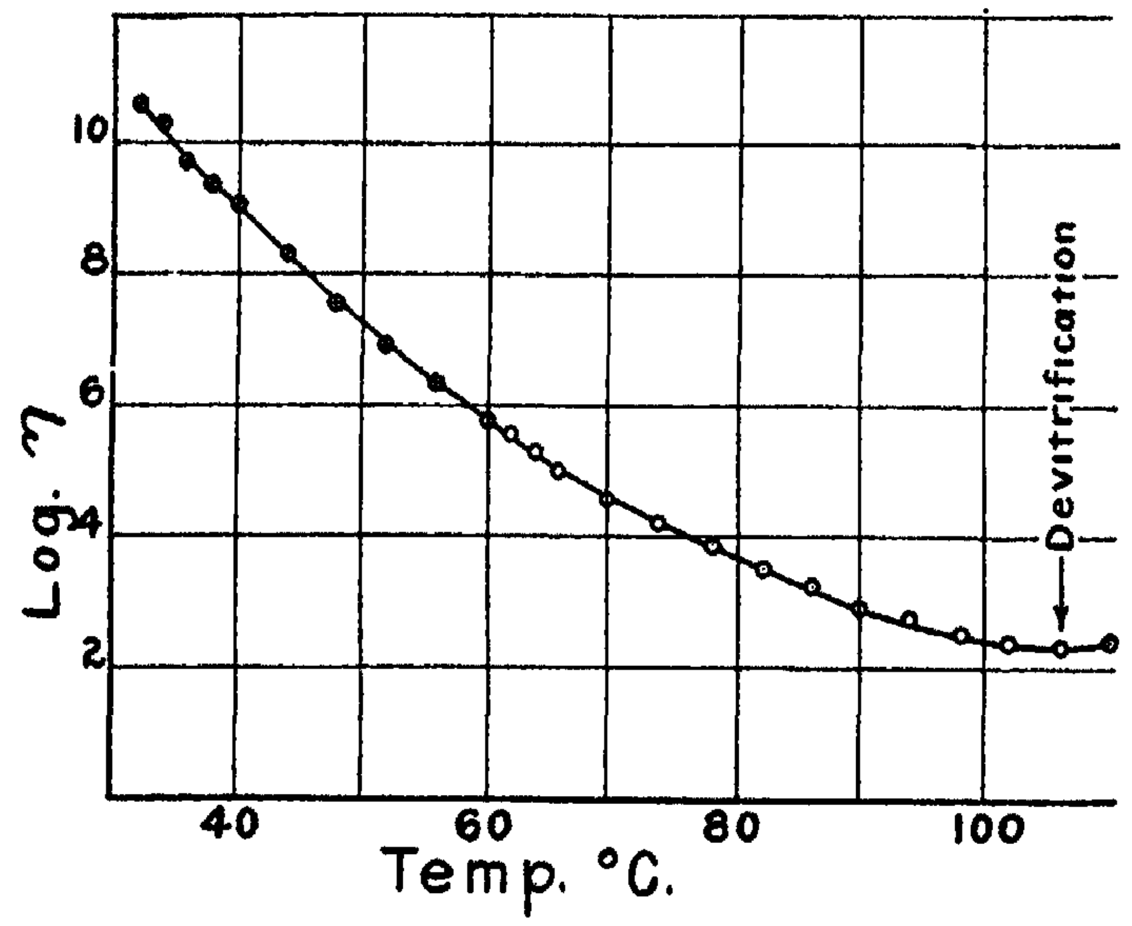

Fig. 3

TABLE III

Viscosity for Liquid Glucose above 60°C

Temp. °C.	η (poises)	$\log_{10}\eta$	Temp., °C.	η (poises)	$\log_{10}\eta$
60.0	5.89 (10^5)	5.770	86.0	1.77 (10^3)	3.248
62.0	3.94 "	5.596	90.0	8.00 (10^2)	2.903
64.0	2.11 "	5.324	94.0	5.85 "	2.767
66.0	1.03 "	5.013	98.0	3.27 "	2.515
70.0	3.84 (10^4)	4.584	102.0	2.45 "	2.389
74.0	1.67 "	4.223	106.0	2.09 "	2.320
78.0	7.49 (10^3)	3.875	110.0	2.45 "	2.389
82.0	3.15 "	3.498			

included the data for Sample III obtained with the first viscometer. The two sets of data are in good agreement and thus give us an experimental curve for a liquid range of about 80°.

Viscosity Data for Glucose-Glycerol Solutions.—Viscosity measurements in the range between 10^6 and 10^{11} poises were made upon various two-component liquids in the two systems, glucose-glycerol and glucose-"97% glycerol." The essential data for the first system are given briefly in Table IV. In Column I are the various viscosity values in even numbers, while in the succeeding columns appear the temperatures corresponding to these values for the several liquids of the system. In the case of each liquid these results were derived from a graph in which log η was plotted against the temperatures of the measurements. The "hardening point," corresponding to a viscosity of 10^{13} poises, was obtained by extrapolation.

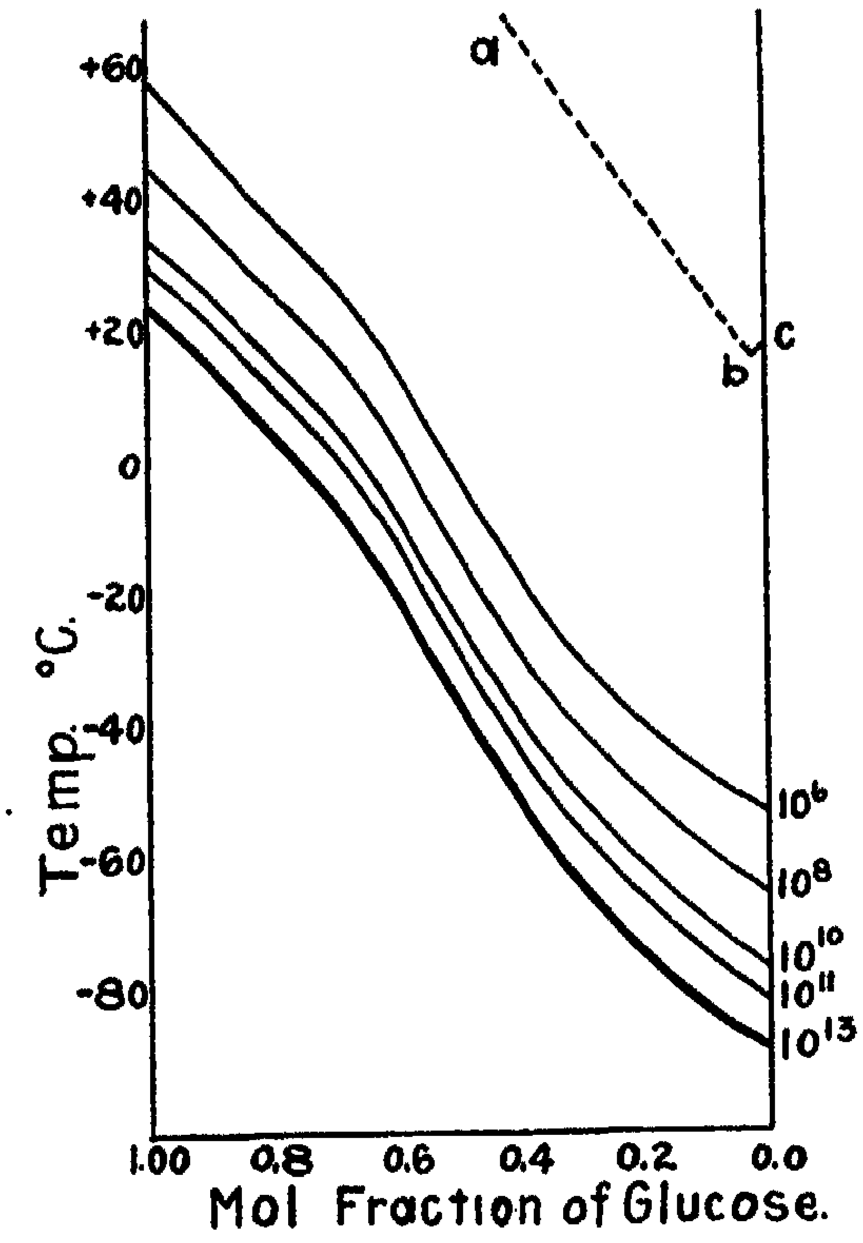

Fig. 4

The high-viscosity isokoms for the binary system, glucose-glycerol.

The isokoms (i.e. lines of constant viscosity) for this system are represented graphically in Fig. 4, where temperatures are plotted as ordinates against the mol fractions as abscissas. The very heavy line for a value of 10^{13} poises might be called the "hardening line" or boundary between the liquid and glassy regions. It falls far below the broken line abc which represents approximately the position of the equilibrium lines between the liquid phase and phases of pure crystalline glucose and pure crystalline glycerol, respectively. This last line has not been realized experimentally but was sketched into the figure after the eutectic temperature had been calculated for this system by the method of Washburn and Read.[1]

Table IV

Viscosity Data for the Glucose-Glycerol System

Viscosity in poises	Mol Fraction of Glucose in Solution					
	1.00	0.80	0.60	0.40	0.20	0.00
10^6	58.4°C.	38.0°C.	14.0°C.	−16.0°C.	−37.°C.	−52.°C.
10^7	51.6 "	33.0 "	8.0 "	−22 "	−42 "	−58. "
10^8	45.6 "	27.6 "	3.0 "	−28. "	−47. "	−64. "
10^9	40.0 "	22.5 "	− 2.0 "	−33. "	−53. "	−70. "
10^{10}	35.1 "	17.5 "	− 7.5 "	−38. "	−59. "	−75. "
10^{11}	31.0 "	13.0 "	−12.0 "	−43. "	−63. "	−80. "
10^{13}	25. "	6. "	−20. "	−50. "	−72. "	−87. "

Essentially similar results were obtained in a study of the system glucose-"97% glycerol." As compared with the first system containing anhydrous glycerol, the only effect of 3% water in the glycerol was to lower the temperatures corresponding to the various viscosity values, the effect being greatest, of course, for the sample of 97% glycerol itself. In this particular case the "hardening point" was lowered about 5°.

Summary

The viscosities of undercooled liquid glucose have been measured over a temperature range of almost 80°. Five different samples of glucose gave slightly different curves as the "hardening point" was approached, probably owing to varying proportions of the α and β forms in these samples as well as to small but variable amounts of water. From a study of the data the *hardening point* was rather arbitrarily defined as the temperature at which an extrapolated viscosity value of $10^{13.0}$ poises was found. For glucose it is about 25°C.

The viscosities and "hardening points" for various liquids in the two binary systems, glucose-glycerol and glucose-"97% glycerol," have been determined.

Department of Chemistry,
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April 14, 1929.

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[1] Washburn and Read: Proc. Nat. Acad. Sci. 1, 191 (1915). In this calculation the binary system was assumed to be ideal and the heats of fusion of glucose and glycerol were taken as 7,800 and 4,370 cal. per mol, respectively. The eutectic temperature and mol fraction of glucose thus obtained were 17.0°C. and 0.016, respectively.

THE LOWEST TEMPERATURES AT WHICH OXIDES SHOW REDUCTION BY HYDROGEN*

BY J. L. ST. JOHN**

An extended research was carried out by Wright, Luff and Rennie[1] on the reduction of a number of oxides by hydrogen and other reducing agents. They found that during reduction there was first an "incubation" period, which increased in length as the temperature was lowered, followed by an "induction" period during which the rate of reduction increased to a maximum. Thereafter the rate decreased as the reduction neared completion. M. W. Johnson[2] concluded that the higher either of the reacting bodies is previously heated the higher is the reduction temperature. He believes that in reducing a compound there are two forces which must be overcome, a chemical force, which is constant for any one compound, and a physical force which varies with the complexity of the molecule and is affected by the previous heat treatment which profoundly modifies the physical nature of the reacting bodies. Rogers[3] concludes that zinc oxide in contact with copper oxide is completely reduced in six hours by hydrogen at 300°C. Pease and Taylor[4] believe that adsorbed water is partly responsible for the incubation period postulated by Wright, Luff, and Rennie.

This investigation was undertaken to determine the lowest temperature at which oxides show an appreciable reduction with hydrogen, measured by the weight of water evolved. The reduction tube consisted of a glass tube of medium thickness about 45 cm. in length and 2 cm. inside diameter. This was bent near the center to form an angle of 145°. A boat containing the oxide was placed in the shorter limb which was held in a horizontal position. A thermometer, extending through a stopper in the longer limb of the tube, was imbedded in the oxide so that the temperature recorded was that of the mass itself. Electrolytic hydrogen was passed through a solution of potassium pyrogallate and dried by passing over calcium chloride, through sulfuric acid, and finally over phosphorus pentoxide. It was led into the reduction tube through the stopper carrying the thermometer. A glass-stoppered U-tube containing phosphorus pentoxide was connected to the exit end of the reduction tube to absorb the water formed by reduction. Return of moisture into the U-tube from the air was prevented by a calcium chloride tube. The oxide was weighed into the boat from a desiccator. It was placed in the reduction tube, heated to 110°C with a stream of dry hydrogen passing over it,

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* Contribution from the Chemistry Laboratory of Purdue University. The author wishes to express his appreciation to Dr. J. H. Ransom for his interest and suggestions.

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[1] Wright, Luff, and Rennie: J. Chem. Soc., 33, 540 (1878); 35, 475 (1879).

[2] Johnson: Trans. Am. Inst. Mining Engineers, 47, 219 (1913).

[3] Rogers: J. Am. Chem. Soc., 49, 1432 (1927).

[4] Pease and Taylor: J. Am. Chem. Soc., 43, 2179 (1921).

allowed to cool and reweighed. This was repeated to a constant weight. On the basis of the results of Pease and Taylor, this procedure would tend to reduce the length of the "incubation" period suggested by Wright, Luff and Rennie. The reduction tube containing the boat was again heated to 110°C and allowed to cool with the hydrogen passing through. The U-tube was then closed and weighed. This procedure was necessary to remove the last traces of moisture from the oxide and to sweep out all moisture from the reduction tube after opening it to the air.

With the boat and U-tube at a constant weight dry hydrogen was passed through the system and the boat was heated to some definite temperature for one hour. The boat was then allowed to cool in the stream of hydrogen and when cool both boat and U-tube were again weighed. Reduction would be shown by a loss in the weight of the boat with an equivalent gain in the weight of the U-tube.

Using C. P. copper oxide, it was found that there was an appreciable reduction at 140°C to 141°C while no appreciable reduction could be detected at 139°C. At temperatures above this there was an increasing amount of reduction per unit of time as higher temperatures were used until at 190°C there was a comparatively large amount of reduction in twenty minutes. After reduction at 145° the surface of the oxide had a perceptible copper-like appearance.

Work with other oxides showed temperatures at which reduction could be detected as follows: zinc oxide 310°, lead monoxide 185°, cadmium oxide 280°, arsenic trioxide 185°.

After temperatures of initial reduction had been determined for copper oxide and zinc oxide a calculation of the temperature at which the other oxides should show an appreciable reduction was made on the assumption that there was a relation between these temperatures and the heat of formation of the oxides. Taking the heat of formation of copper oxide as 37,160 (Landolt-Börnstein's Tabellen) and zinc oxide as 85,000 it is calculated that for every 281 calories additional heat of formation there is a rise of one degree in the temperature of initial reduction. On this basis we would expect lead monoxide to reduce at 187°C, arsenic trioxide at 192°C, and cadmium oxide at 240°C. The agreement of the temperature of reduction found with the calculated temperature is very good in the case of the lead monoxide and the arsenic trioxide. In the case of the cadmium oxide the temperature determined experimentally is somewhat above that calculated. This may be explained on the basis of M. W. Johnson's work by the fact that the cadmium oxide used was freshly prepared in the laboratory and was heated to a temperature of approximately 700°C during preparation and the temperature of initial reduction thereby raised.

Rogers' temperature of 300°C for zinc oxide is close to our temperature of 310°C for the initial action. He explains his reduction at this temperature by assuming a catalytic action of the copper oxide mixed with his zinc oxide. Since he exposed his oxides to hydrogen for six hours a fuller explanation can be offered in the light of our results and those of Wright, Luff and Rennie. We found that zinc oxide will reduce at these temperatures and Rogers simply ran his experiment a sufficient length of time to carry it through both the "incubation" and the "induction" period, whence it continued to completion with comparative ease. Rogers does not mention having tried zinc oxide alone by this method.

Pease and Taylor, using an air-dried copper oxide, reduced the incubation period at 150°C to about half the normal length which they state is one to one and a half hours. By our method of pre-drying we reduced the incubation period to less than one hour at 140 to 141°C where we obtained appreciable reduction of the copper oxide.

Summary

The temperature at which several metallic oxides first show an appreciable reduction with hydrogen has been determined. A relation between the temperatures of initial reduction and the heats of formation of these oxides has been suggested.

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SEVENTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS*

ENZYME CATALYSTS

BY E. F. ARMSTRONG AND T. P. HILDITCH

It has been the practice in these reports, whilst indicating the general progress in the knowledge of contact catalysis, to stress certain aspects of the subject in particular. For many of us, the ultimate aim of our strivings to understand the phenomena of nature is to gain some clearer understanding of the facts of life as portrayed by the chemical actions in the living cell. It has long been appreciated that, in such, catalytic agents play a leading, if not all-important, part and it is proposed therefore in this report to take stock of our knowledge of the catalysts of the cell.

The parallelism between inorganic catalysts and those involved in metabolic processes has been the subject of remark for rather more than a century. At times it has been held by some that the two divisions of chemical action have little or nothing in common beyond certain superficial resemblances; others have maintained the opposite view, and believed that fermentation and inorganic catalysis were varying instances of the same mode of operation of chemical activity. We are concerned at the moment rather to examine in some little detail various aspects of either class of phenomena in order to define with some clarity points of resemblance or of dissimilarity.

From the point of view of the chemist, vital changes are a series of balanced actions, generally reversible, following one after the other, which are only very crudely expressed by the chemical equation indicating the initial and final products of the reaction. Few, other than those who are really wedded to this field, realise how very delicate this balance is and how elaborate is the mechanism which is controlled apparently by those subtle agents for which the general name "enzymes" is used. These, the catalytic agents of protoplasm, determine the sequence and the magnitude of the molecular changes which distinguish living from dead matter and which include the biological synthesis of compounds, complicated or relatively simple, from carbon dioxide, water and nitrogen, and also actions of decomposition, for example, hydrolysis, oxidation (combustion) or reduction.

Apart from the complexity of the changes which proceed in the living cell, the fact that the study of these actions has been prosecuted most often from the point of view of physiology or pathology has involved a viewpoint

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distinctly different from that of the student of the more conventional catalytic actions. In consequence it is not too easy to detect, in the extensive literature on enzyme action, information which is pertinent to the general question of the behavior and function of the actual catalyst. Re-direction of research on enzyme action in the sense indicated, and in the light of modern work on contact actions at the surface of inorganic catalysts, is important not only with reference to the development of biochemistry, but also in its possibilities as regards more frequent utilisation of enzymes in the field of applied organic chemistry. The recent advances in the biochemical production of butyl alcohol, acetone, glycerol, aldehyde, and lactic acid can undoubtedly be supplemented by those of other compounds; as is well known, there is scope for improvement and modernisation in the bacterial production of butyric and of citric acids, both of which are in increasing demand.

Our exact knowledge of the factors which affect the activity of enzyme catalysts is barely 25 years old. Since the broad character of these reactions and their general simplicity was first established, many papers have been published, to a large extent without reference to and apparently without knowledge of the earlier work, which have done much to obscure the subject.

Without going into detail, it can be concisely stated that the factors controlling the rate of enzyme action[1] are:—

1. The amount of the catalytic agent.
2. The concentration of the substrate upon which it acts.
3. The presence of substances which reduce the effective surface of the catalyst.
4. The influence of the products of change as depressants of a similar nature.
5. The acidity or hydrogen-ion concentration of the medium in which the amphoteric enzymes act.
6. Dehydrating agents affecting the inhibition and water relations of the catalyst.

It has been shown that the shape of the time curve expressing the hydrolysis of cane-sugar by invertase is ideally linear,[2] and that alterations in the rate of change leading to less simple relationships (frequently of a "logarithmic" character) are associated with subsidiary effects involving change in the effective activity of the enzyme. Association of one or more of the products of change with the enzyme is a common occurrence affecting the rate of action.

The amount of enzyme and substrate in combination at any one moment has been defined as the active mass. This conception has enabled a simple explanation of the time/change curves of enzyme activity to be given, including both the initial linear period, the subsequent logarithmic period and the final stages in which the rate of change is still slower. It cannot be too strongly emphasised that all more complicated mathematical equations to express the velocity constant throughout an enzyme change are unnecessary and fallacious.

The general features of the rate of change have led to the view that enzyme action takes place entirely at the surfaces of colloid particles suspended in the solution of the substrate and not between substances which are all in true solution.

Before discussing further the progress of a typical enzyme action and the susceptibility of the enzymic catalyst to alteration in activity by reason of the causes enumerated above, we may pass on to consider the evidence at present available as to the actual nature of enzymes. The statement that these act in the form of colloidal particles recalls the converse attitude taken by Bredig,[3] who termed the dispersions or sols which he prepared from platinum and similar metals "inorganic ferments," on account of their similar behaviour to the "catalase" group of enzymes in effecting chemical actions such as the decomposition of hydrogen peroxide. The resemblances between a metallic sol and an enzyme are, however, of a somewhat superficial nature. Apart from the great complexity of chemical structure and the marked specificity in action which are the outstanding marks of the natural enzymes, the rate of action of Bredig's colloidal platinum is not of the same order as those of most of the usual preparations of enzymes, and falls far short of those of the relatively concentrated enzyme fractions prepared by Willstätter and his colleagues during their well-known recent investigations.

Since the most highly active fractions obtained are stated by these workers to have been still far from 100 per cent. enzyme, it follows that the metallic sols cannot be compared in any quantitative degree with the enzymes. Yet, from a qualitative point of view, the two classes of catalysts, are similar not only in certain aspects of chemical behaviour but also with reference to their temperature relationships. Ernst[4] showed that colloidal platinum sols are closely parallel to the enzymes in this respect, possessing a comparatively low optimum temperature of more or less sustained activity, whilst showing greater initial, but more fugitive, activity at temperatures above the optimum; until a point is reached at which the catalytic power is suppressed completely. These phenomena are to be connected in both cases with changes effected by temperature in the colloidal surfaces, which are ultimately "coagulated" or altered so that the power of catalysing chemical actions disappears.

Whilst we may suppose, therefore, that so far as physical condition goes the enzymes are comparable most closely to metallic sols in the realm of inorganic catalysts, it is well to bear in mind that other analogies subsist between them and the more closely studied class of solid surface catalysts, notably the metals and metallic oxides.

In the first place, the similarity in regard to temperature effects is still present, the outstanding differences being the generally wider range of temperature over which the activity of a solid contact agent is exhibited and the fact that the working range of temperature of the latter is usually much higher than in the case of the natural enzymes. Finely-divided nickel, for instance, commences to show catalytic power below 100°C., its optimum range in hydrogenation is usually about 140–180°C., and above about 350°C. its activity (in the absence, of course, of special "supports") is soon suppressed.

Further, the so-called "promoter" or stimulant action of many substances on solid contact agents, and more especially the behaviour of mixed catalysts, are matters which it is interesting to note for comparison with the behaviour of enzymes. Readers of these reports will be well aware that the precise mechanism of catalyst stimulants and mixed catalysts is as yet far from perfectly understood. Willstätter, in his Faraday Memorial Lecture,[5] refers to the possibility that a mixture of two components, whether by deformation of electron orbits or alteration of "affinity fields,"may result in a new catalyst having an "enzyme-like specificity and potency comparable with that of homogeneous compounds," and proceeds to a possible analogy between such mixed catalysts and many enzyme systems which are known to be composed of more than one enzyme and to act differently from any one of the individual enzymes present.

It is well to remember, however, in this connection that there are two well-defined classes of mixed solid contact agents; in one case, an added component serves to increase the activity or potency of the original catalyst for effecting one and the same chemical change, whilst in another category we find a mixture of catalysts* which may induce a decomposition which either component alone fails to bring about (the action of "Hopcalite"[6] in the oxidation of carbon monoxide at low temperatures is a good example of this class). The first-mentioned type, in which the specific activity of the original catalyst is merely accentuated by the presence of the added material, is much the more common, and there is considerable evidence (for example, the stimulating action of alumina or magnesia on nickel in hydrogenation)[7] for the view that here the cause of the enhanced activity lies in something akin to more profound subdivision (i.e., greater effective surface) of the actual catalyst particles.

Again, the enzymes are well-known to be essentially specific in their action, a fact which indicates some close connection in molecular structure between them and the substrate on which they act. There is some little danger that the stress laid on the specificity of enzymes may be misleading if it is not carefully defined. Enzymes differ widely in the specific nature of their action. Some of the varieties of lipase, for example, are capable of hydrolysing a comparatively wide range of compounds belonging to the class of esters, and in particular they appear to act more or less indiscriminately on the fats irrespective of the particular nature of the fatty acids present. On the other hand, maltase, emulsin and most of the proteoclastic enzymes are far more specific, since most frequently they are only able to effect change in compounds of very definite stereochemical configuration, and it is in this respect that they are most differentiated from the solid contact agents.

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* Professor Frazer of the Johns Hopkins University reports that he has succeeded in purifying certain of the oxide catalysts to such a degree that they are quite as active as, if not more active than, the mixture of oxide catalysts known as Hopcalite.

Equally, it must be borne in mind that inorganic (non-enzymic) catalysts are also highly specific in that the course of the action depends on the catalyst employed; enzymes share this property, but also, in many cases, possess the additional property of only being active with respect to certain members of a given class of compounds whose configuration, it may therefore be assumed, is compatible with that of the enzyme.

In the case of certain enzymes, substances which have similar structure to the substrate act to retard change though they cannot be hydrolysed by the enzyme—for example, the hydrolysis of the sugar maltose and of α-glucosides by the enzyme maltase of yeast is retarded in presence of glucose or of α-glucosides.[8] This is in itself further proof that some form of combination of a chemical rather than a physical nature takes place between enzyme and substrate prior to hydrolysis. This corresponds with the addition-compound theory of catalysis which has found acceptance in connection with the action of nickel and other metallic catalysts.

To avoid any confusion of thought as to the specificity which characterises solid contact agents, attention may be drawn to a few very obvious cases. Probably the most useful example is the old one of the varying results obtained when alcohol vapour is exposed to the action, on the one hand, of nickel, copper or a similar metal, and, on the other, of oxides such as alumina or theoria.[9] The two groups of catalysts exert specific influences respectively of dehydrogenation or dehydration. Furthermore, Sabatier's classical work on the catalytic behaviour of a whole range of metallic oxides[10] will be recalled, wherein the specific action produced varies, according to the particular oxide, over the range exclusive dehydration—mixed dehydration and dehydrogenation—exclusive dehydrogenation.

Another familiar instance is the varying action on a mixture of carbon monoxide and hydrogen of different catalytic compounds: nickel, palladium, or platinum cause the production of methane[11] (with carbon dioxide under certain conditions), zinc oxide or mixed zinc-chromium oxides[12] yield methyl alcohol almost exclusively, and iron in presence of alkaline oxides[13] furnishes a mixture of hydrocarbons, alcohols and other products.

It is possible to point to other actions of solid catalysts which, although not comparable with the stereochemical selectivity of the enzymes, are of a still more specific nature than those just cited. For example, hydrogenation of an isolated ethylenic linkage in a normal aliphatic chain (as in oleic acid) is accompanied by the production of some of the geometrically-isomeric form of the original ethylenic derivative, together with that of isomeric compounds containing the ethenoid or double bond in positions adjacent to that originally occupied;[14] and it is reported that palladium (and, possibly, copper) yields higher proportions of the isomeric forms than does nickel when employed as catalyst. The studies of Adkins[15] and his co-workers on the different types of catalytic change induced by alumina prepared in different ways is another instance of pronounced selectivity in the action of an inorganic catalyst. Again, Willstätter[16] has stated that hydrogenation of naphthalene in presence of platinum yields exclusively *cis*-decahydronaphthalene, whilst with nickel the chief product is the *trans*-compound; and similar results have been reported in connection with the methylcyclohexanols and menthols produced in the hydrogenation of cresols and thymol. Most striking of all, perhaps, is the phenomenon of selective hydrogenation,[17] whereby, in some cases, one of a number of ethylenic linkages is hydrogenated preferentially, to the almost complete exclusion of the rest; or, in other cases, hydrogenation of, for example, a diolefinic compound proceeds in such a way that mono-olefinic derivatives are formed before any notable amount of saturated substance appears, although either of the original double bonds may be and are attacked (leading to a mixture of mono-ethylenic isomerides). The work of S. Lebedev[18] and his colleagues has shown especially well the conditions which determine selective action of this kind in some cases; and stress has been laid by these investigators upon the great influence on the course taken by the hydrogenation of the presence of substituent alkyl groups.

The examples quoted of variation in the proportion of geometrical isomerides formed during hydrogenation and of the influence of substituent alkyl groups (i.e., branched-chain configuration) on the course of selective hydrogenation will be admitted to approach somewhat towards the still more delicate stereochemical relationships which are apparent between some enzymic catalysts and their substrates.

Consequently, when Willstätter, in his Faraday Memorial Lecture which has already been mentioned, says "there appears to be a deep gulf between the inorganic catalysts and the enzymes" (adding the further statement "In reality this gulf has already been bridged by accurately-defined organic compounds which act like enzymes"), it would appear that something less than justice is done to the analogies already existing between the two classes of catalyst. From a general standpoint, almost all the chemical transformations effected by enzymes are capable of being paralleled, in greater or smaller measure, by analogous transformations which are realised by one or other of the inorganic catalysts.

We can go somewhat further than this, however, if we consider the few cases of "accurately-defined organic compounds" which have been investigated from the point of view of catalytic action. In the first place, Willstätter has demonstrated that some of the natural complex products of or interveners in vegetable and animal metabolism possess catalytic properties somewhat similar to enzymes, although they are by no means enzymes in the usual sense of the term. Chlorophyll, according to Willstätter and Stoll.[19] may build up carbohydrates from carbon dioxide by rearrangement of the latter (under the influence of radiation) in the form of the labile chlorophyll-carbon dioxide complex. Willstätter and Pollinger[20] have found that oxyhaemoglobins from different animal species behave like feeble peroxydase, and vary in activity according to their source. Kuhn and Braun[21] have established further that, when haemoglobin is resolved into its components, the resultant haemin has no peroxydase properties, but shows distinct catalase activity. This is almost direct evidence that the specific action of organic-compound catalysts depends on the chemical constitution of the latter.

Another line of argument may be based on the well-known synthetic agents for the hydrolysis of fats which were developed originally by Twitchell,[23] who condensed benzene or naphthalene with oleic acid by means of sulphuric acid and obtained a product containing one or more free sulphonic acid groups united to the oleic acid by means of the aromatic nucleus. Many variants of the original agent have been proposed, and latterly sulphonated petroleum hydrocarbons of certain types have been suggested. All these contact agents have in common the presence of a strongly hydrophilic sulphonic acid group united with a hydrocarbon or fatty acid residue of high molecular weight. Consequently they may be supposed to exert marked affinity both for fats, fatty acids and water, whilst the actual hydrolysis is conditioned by the presence of the highly active sulphonic acid radical present in the complex. The Twitchell agent is, in fact, probably the nearest synthetic approach which has been made to the production of an artificial compound with properties and structure resembling in essentials those of a natural enzyme.

Summing up all these analogies and inferences, it seems that there is good ground to come to the following conclusions:—

1. The enzymes exert hydrolytic action in virtue of the presence of definite chemical groupings adapted to form intermediate complexes with the substrate and water or other interactant.

2. They owe their specific powers (especially those connected with stereo-isomeric conditions) in all probability to their own asymmetric configuration as natural synthetic products.

3. Many general analogies can be traced between the recognized behaviour of inorganic contact agents (especially those operating on liquid media) and that of enzymes.

4. From a physical point of view, they are most nearly similar in general properties to the dispersed sol forms of inorganic catalysts; but the existing evidence goes to show fairly conclusively that their superior activity and delicacy of action cannot be accounted for simply by differences in the degree of dispersion.

All this of course is only one side of the possible nature of an enzyme. We have still to consider their formation in the cell and the development of their catalytic powers, together with other phenomena characteristic of enzymes. Amongst the latter, the influences exerted by "co-enzymes" and "anti-enzymes" are respectively analogous to the inorganic catalyst promoters and poisons. Substances toxic to either group of catalysts probably act in a similar manner, the primary cause being in both cases selective adsorption of the toxic compound by the catalyst with resulting exclusion of most or all of the material to be acted upon from the catalytically active centres. With enzymes, however, it usually happens that some of the products of change are themselves prone to enter into association or be strongly adsorbed by the enzyme, and consequently the apparent activity of the latter frequently declines as the products of change accumulate in the system. This state of affairs has rarely been encountered so far in the case of most actions at the surface of solid contact agents, but it has been met with in several common instances of homogeneous catalysis: for example, in some cases of chlorinations of liquid organic compounds in presence of "carriers," and in the Friedel-Crafts synthesis wherein, as shown by Steele,[23] the aluminium chloride forms more or less definite complexes with the original hydrocarbon, the organic halide, and the hydrocarbon produced in the interaction.

The part played by "co-enzymes" is not quite so closely parallel to the ordinary case of promoter action in inorganic catalysts. It is, indeed, by no means agreed as to what the precise function of a "co-enzyme" is, but the main distinction between this type of substance and a catalyst promoter is that, whilst the latter is an aid to the development of more potency, the "co-enzymes" are indispensable for the progress of many enzyme actions. The mechanism by which co-enzymes act is little understood at present. The presence of a suitable electrolyte in appropriate concentration seems to be the chief factor in some cases, but in others the mere presence of a simple salt is not sufficient; thus zymase is not restored to activity by the simple presence of a phosphate solution, although phosphates are necessary. There is reason to suppose, with Harden,[24] that the real co-enzyme is in this case a hexose-phosphoric-acid ester. It is further possible that, in some cases, the "co-enzyme" is a substance which activates or releases the enzyme itself from a still more complex pre-existent compound in the cell.

As is well-known, the activity of enzymes is peculiarly susceptible to the acidity or hydrogen-ion concentration of the medium in which they act. This is one of the most prominent distinctions between enzymes and inorganic catalysts, but it may be remarked that, even in this respect, analogies are not lacking between the two classes. The action of nickel as a hydrogenating catalyst, for example, has been shown to be greatly influenced by the general reaction of the compound hydrogenated; this is shown most clearly, perhaps, in the increased ease of hydrogenation of phenols in presence of a small, optimum concentration of sodium carbonate, and again, whilst it is generally recognised that nickel hydrogenates acidic compounds with relative difficulty, it is also probable that basic compounds are less susceptible than neutral compounds to hydrogenation in presence of nickel. At all events, there is some reason to believe that ammonia acts as a catalyst poison towards nickel, and basic ring-systems such as pyridine, pyrrol or quinoline are notoriously difficult to hydrogenate by comparison with benzene or naphthalene. Another example of acidity controlling rate of action is due to the recent work of Conant and Brammann,[25] who have observed variations of a millionfold in the rate of acetylation of naphthol by acetic anhydride as a result of varying the acetic acidity of the reaction medium.

The exact bearing of the optimum hydrogen-ion concentration on the activity of an enzyme has yet to be understood. Nearly all enzymes are very sensitive to slight changes in the acidity or alkalinity of the solution and are most active only at a definite hydrogen-ion concentration; the most effective value of the latter varies according to the enzyme, the usual range being from media slightly more acid to media slightly more alkaline than pure water. Enzymes are, as a rule, of an amphoteric nature and doubtless this has considerable relation to their activity over only a limited range of acidity and their maximum activity at a definite hydrogen-ion concentration. As colloids they are susceptible to heat and their structure is impaired or destroyed at moderate temperatures.

The work of Willstätter and his school on the attempted isolation of various enzymes has afforded definite results of an important character, but no enzyme has so far been produced in a condition approaching purity. The work has been notable for the degree of utility manifested in successive processes of adsorption and elution carried out with carefully selected agents. It has been proved practicable in this way to separate enzymes from colloidal substances not closely related to them, though beyond this, except by very special procedure, it has not been found possible to go. The ramifications of this research demand that the original papers[26] should be studied by those interested in the details of the procedure. Here it must suffice to cite the separation of the enzymes of pancreas as an instance. If the mixture is treated with the stable gel form of aluminium hydroxide ("γ-alumina"), lipase present is adsorbed and can be removed by elution of the alumina with a solution of feebly alkaline phosphate; amylase and trypsin remain, and the latter is selectively adsorbed by kaolin.

In the same way, it has been shown that invertase can be almost completely freed from carbohydrates, proteins and phosphorus compounds, with an accompanying increase in activity of the order of over three thousandfold. Proteins are also believed to form no essential part of the lipoclastic enzymes and the peroxydases.

An especially interesting case is that of the vegetable peroxydases, which in the hands of Willstätter and Stoll[27] yielded a concentrate containing a good deal of carbohydrate (sugars) and a definite iron content of about 0.5%. Further purification by selective adsorption led to a still more active preparation of the enzyme, but the sugar constituents disappeared in the process and the iron content diminished to 0.06%. Thus, whilst it appears certain that the carbohydrates present were merely accompaniments to the enzyme itself, it is also doubtful how far the presence of combined iron is necessary. The interesting observation was made that, in the highest stages of concentration reached, the active material assumed a reddish-brown colour reminiscent of that of the porphyrins.

Keilin[28] has recently published a very important contribution on the respiratory processes of cells of aerobic organisms, vegetable and animal, and has given definite proof that the material responsible for at least one portion of the complicated respiratory mechanism of the cell is a widely distributed respiratory pigment, cytochrome, which is composed of three haematin compounds (a′, b′ and c′) and an unbound heamatin compound similar to the protohaematin of haemoglobin. These haematin compounds are responsible for the thermostable peroxydase action, which is shown by the oxidation of various chromogens, such as benzidine, guaiacum, and *p*-phenylenediamine, in presence of hydrogen peroxide. Keilin's work seems to be conclusive evidence at last of the general nature of the peroxydase class of "enzymes," and indicates that "peroxydases" are identical with certain types of the complex organic compounds known as haematins—these "enzymes" at least may now be claimed to be complex carbon-compound catalysts. Whether the hydrolytic and other classes of enzymes will in course of time be proved to be equally definite entities remains to be seen. Quite possibly a difference may be revealed in that, whilst a specific haematin (peroxydase) may be capable of promoting oxidation processes with reference to a comparatively wide variety of compounds, a process such as hydrolysis of a particular compound may demand the presence not merely of a suitable hydrolytic mechanism but of such a mechanism so arranged in conjunction with the rest of a complex molecular system as to satisfy configurational or other intramolecular requirements.

Not the least interesting part of recent biological work is the differentiation made between certain features which are shown to be characteristic of the enzyme itself and other very characteristic features of enzyme action which are equally shown to be due to the influence of other compounds present with the enzyme. Thus the lipase of the human pancreas is most active in an alkaline medium, whilst that of human gastric juice is most active under feebly acidic conditions (pH 5–6); when the latter is submitted to the adsorbent action of kaolin, however, some compound (or compounds) is removed and the reaction of the enzyme is transferred to an optimum on the alkaline side at pH 8.[29] The optimum hydrogen-ion concentration for a given enzyme would thus seem to be dependent, not on the ultimate enzyme alone, but on the accompanying components of the complex mixture or system on which the term natural enzyme is at present conferred.

On the other hand, the specificity of any enzyme has so far been found to remain unchanged throughout any concentration process which has been applied and in spite of exceedingly great increases in the relative activity of the purified enzyme and the original material. This holds for examples of selective stereochemical action in the cases of invertase, maltase, etc. and of certain animal lipases which hydrolyse the *d*- and *l*- forms of certain optically-active esters at unequal rates;[30] and it may therefore be inferred, from the present experimental evidence, that the selective chemical and configurational action of enzymes is an essential property of the catalyst itself.

Another development has suggested that some enzymes (e.g., trypsin) only exhibit their full activity when released or stimulated by a specific type of complex associated with them (e.g., the kinases). Kinases were formerly supposed by Bayliss and Starling[31] to be themselves enzymes which in the first place converted an inactive complex "trypsinogen" into the enzyme trypsin; according to Willstätter,[32] trypsinogen is itself an enzyme of relatively feeble activity which, when associated with an activator or "co-enzyme" of the kinase group develops much greater potency. This explanation is based on adsorption experiments whereby, employing casein precipitated *in situ* as adsorbent, the kinases can be removed, leaving all the trypsin in solution.

It is perhaps permissible to attempt to sum up the evidence presented by the data discussed in the preceding pages in the form of a hypothetical suggestion of what may be the essential parts of a natural enzyme *per se*:—

1. The physical form of the enzyme is that of a dispersed colloidal sol, the colloid molecule probably being of great complexity.
2. As regards the chemical nature of the enzyme molecule itself, it is evident that neither protein, carbohydrate, organic phosphorus nor iron compounds, etc., is necessarily an integral component. Yet it must be concluded that the whole of the molecular complex is unlikely to be involved in the enzymic changes effected in the appropriate substrates, and thus we are reduced to a somewhat vague picture of a large molecule of undefined composition which, however, contains certain groupings of highly specific character and, usually, configuration, which are able to enter into association with specific substrates.
3. At the same time, however, the whole molecule is peculiarly liable to form associated complexes with other large molecular species, and it should be further observed that the presumed reactive groupings must be, if not actually involved in these associations, considerably influenced thereby. For, not only the rate of action, but also the optimum character of the reaction medium, is largely affected by these apparently extraneous complications: only the specific nature of the chemical change effected by the enzyme itself appears to persist unaltered whatever the varying environment, so to speak, of the latter may be.
4. The question of enzyme stimulation or "co-enzyme" activity appears to be closely connected with the combinations with other colloidal molecules to which enzymes appear to be prone. Some instances of the "release" of an enzyme in the cell in the active state seem to be explicable on the theory of intervention or stimulation by association with a co-enzyme; in others this possibility does not seem entirely clear.
5. It appears on the whole that the catalytic properties of an enzyme are at present best interpreted by regarding it as an instance of a catalyst which, for practical purposes, is in a labile or dynamic condition. We do not mean by this that the essential catalyst, the enzyme *per se*, is continually made and destroyed or re-made. It is suggested, on the contrary, that the enzyme itself may well be synthesised once for all in the cell, but that, by its capacity for association or interaction with other products of the cell (whether enzyme stimulants or retarders, or comparatively inert), its activity is peculiarly liable to a variety of delicately-adjusted conditions and is very largely controlled by its environment at any given time.

The properties revealed by the foregoing survey of the present evidence are typical of provision in nature of means whereby a close control over chemical reactions is exercised. The very great activity of enzymes as compared, for example, with mineral acids hardly requires emphasis. The enormous activity of some of Willstätter's partially concentrated enzymes makes possible some idea of that of a pure enzyme, freed or "released" from any of the accompanying complexes of similar chemical character but catalytically inert. The close combination of enzyme and related substrate in a large colloidal complex must set up conditions where a minimum amount of energy is required to bring about change.

In life the enzyme is not normally in a free state—it is only liberated as required. Either the water equilibrium of the cell is such that no simple water molecules are available to complete the hydrolytic circuit so that before action begins dilution must take place. This can be effected by the entry into the cell of a stimulant or hormone such as is controlled by the nervous system. Alternatively, the enzyme itself is not in the free state and must first be liberated from a complex colloid by another enzyme. A third possibility is the need of a co-enzyme, as for example the cozymase of cell-free alcoholic fermentation.

Thus far we have mainly focussed our attention on the nature of the enzymic catalyst and, to some extent, the general mechanism of its action. It remains to direct the notice, particularly of organic chemists, to the chemical changes involved in the course of synthesis and decompositions in the living cell. The lacunae in our chemical knowledge here are colossal. Investigations into such matters are admittedly most difficult; but the possibilities are extraordinarily inviting, and work such as that of Neuberg[33] and others on the alcoholic fermentation of glucose and fructose indicates that the problems set are not by any means completely insoluble.

Practically the only actions of enzyme chemistry which have been intensively studied are cases of simple hydrolysis or (conversely) withdrawal of the elements of water. The chemical changes whereby chains of carbon atoms are assembled or disrupted in nature have not yet been studied from the standpoint of organic chemistry, if we except the instances of possible stages whereby carbohydrates are built up from a formaldehyde complex, and the work, just mentioned, on the degradation of hexoses into alcohol, carbon dioxide, etc., by fermentation (together with recent related work by Langwell and others[34] which elucidates to some extent the possible transitions which take place when cellulose or sugars are submitted to the action of certain bacteria).

The manner in which sugars, and perhaps other materials, are built up into fatty acids, and the latter assembled into glycerides (neutral fats) of specific constitution; the evolution of the numerous types of protein-matter; the disruption or further transformation of the three main classes of natural organic compounds—carbohydrates, fats, proteins; the production of terpene (or isoprene) derivatives—all these await interpretation in terms of organic chemistry. All that is available at present in many cases is a facile "paper" explanation wherein methyl (or other alkyl) groups, hydroxyl radicals, etc., are lopped off at will, unsaturated centres are similarly transposed, eliminated or introduced, and, in general, a scheme of things is envisaged by the biochemist which, if it were realisable in the laboratory or the factory, would open up joyous vistas to the technical synthetic organic chemist.

Definite information is badly needed on this side of enzyme chemistry. As already stated, the work is most difficult; the more so, since intermediate stages of the chemical changes in progress will doubtless often involve the production of organic compounds in unusually labile or unfamiliar forms. Thus the pyruvic acid, methylglyoxal, acetaldehyde and even formaldehyde of the laboratory are undoubtedly not identical, as regard physical and chemical properties, with the corresponding compounds which are transitorily produced during the low-energy transformations proceeding in a comparatively dilute aqueous medium in the living cell.

Doubtless this is getting rather remote from the direct problems of contact catalysis, yet it has a very definite bearing on the possibility of extending the use of enzymes in industrial processes. Two general methods are discernible in the latter connection.

The older one, which is obviously capable of much wider extension, is to select a culture of an organism which produces enzymes capable of inducing definite, and sometimes unusual, chemical actions, leading to the production of useful material. This procedure, long applied to the manufacture of vinegar, lactic, butyric and to some extent citric acids, is receiving fresh attention in the latter case and has of course made striking contributions to industrial chemistry in latter years in the lipase process for hydrolysis of fats[35] and, especially, in the modern method of manufacture of butyl alcohol and acetone.[36] It is, in effect, the production of new, or rather hitherto unnoticed, enzymes by the cultivation of special varieties of microflora, and, consequently, falls more within the province of the bacteriologist than the chemist.

The alternative method is to acquire sufficient knowledge of the chemical course taken by an enzyme process and to endeavour to modify its progress by carrying it out in the presence of added chemicals. Two familiar instances will exemplify this method of attack:—

1. The presence of sulphite or of a mild alkali during yeast fermentation of glucose or fructose causes the acetaldehyde (or acetaldehyde complex) transitorily produced to be respectively fixed as bisulphite compound or "dismuted" into alcohol and acetic acid (or polymerized); consequently the elements of hydrogen which would have transformed acetaldehyde into alcohol are utilised otherwise, and glycerol results—a process which has been, and very probably will again be, used on the large scale for the manufacture of glycerine.[37]

2. The chemical course of the butyl alcohol-acetone fermentation has been studied and grounds for believing that butyric acid and acetic acid were intermediary products were obtained. It has further been shown that, within limits, butyl alcohol, acetone and some other alcohols or ketones can be bio-

chemically produced by adding to a fermenting mash (undergoing the *Granulobacter* fermentation) butyric, acetic or other appropriate acid, of course in such quantities that the acidity of the mash does not exceed a prescribed limit at any given time.[38]

Evidently there are possibilities of considerable progress along these lines, and such progress will be the more rapid as the chemical course of enzyme actions receives increasing attention from organic chemists.

We do not go so far as to suggest that in all cases an enzyme process will readily compete with the more usual forms. The great advantage of low heat consumption in the actual process may be offset sometimes by the difficulty of maintaining an appropriate organism in existence, or by the dilution at which a particular process must necessarily be carried out, leading to excessive fuel charges in recovery of the products. Several instances in the past few years nevertheless give encouragement to the view that enzyme chemistry is only at the commencement of its technical utilisation.

The aspect of catalysis selected for this report has led to a somewhat more general and diffuse treatment than that given by our predecessors. We make no apology for this, however, but rather claim that we have endeavoured to give as careful a statement as the facts warrant of a somewhat elusive subject, expressed in the simplest possible language. If we have interested any workers on catalysis in the importance and potentialities of enzyme chemistry, considered primarily from the point of view of catalytic action, and if this report attracts fresh investigators to this field of contact catalysis, we shall have attained our end.

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LUMINESCENCE DURING ELECTROLYSIS[*]

BY NEWTON HARVEY

In a recent paper Dufford[1] has referred to the luminescence to be observed at the anode of an aluminium electrode rectifier[2] and has observed a similar luminescence with eight other metallic anodes and a number of electrolyte solutions,[3] and also a luminescence with the Grignard compounds in anhydrous ether at anode or cathode with 500 to 1500 volts. There are other known cases of luminescence during electrolysis, namely, the light observed by Bancroft[4] when halides are electrolysed at Hg and other anodes, supposed to be due to combination of halogen and Hg to form the solid halide, and a luminescence at a metallic cathode when solutions of oxyluciferin and luciferase are subjected to potentials of about 1.5 volts.[5] In this case the nascent hydrogen appearing at the cathode reduces the oxyluciferin to luciferin in a layer next the electrode and the luciferin then reoxidizes in a contiguous layer containing oxygen and luciferase. Luciferin and luciferase are the luminescent substances of luminous animals, light appearing when luciferin oxidizes to oxyluciferin in presence of luciferase. It is suggested that the word galvano-luminescence might be used in referring to luminescences which appear during electrolysis with a galvanic current.

Some unpublished experiments of mine carried out at the Nela Research Laboratory in 1924 indicate an efficiency for this galvano-luminescence of luciferin of 1 to 5×10^{-7}, an order of magnitude comparable to that given by Dufford and too small to have any practical interest. Such a luminescence can be used as a test for active hydrogen. It appears with Pt or Pd surfaces in contact with hydrogen or when Zn, Mn, Al, and Cd metals are placed in a water solution of oxyluciferin and luciferase.

I have recently observed quite a bright luminescence that can be used as a test for active oxygen, formed on anodes during the passage of an electric current and also produced from the decomposition of ozone or H_2O_2. This involves the use of a chemiluminescent compound, aminophthalichydrazid, recently described by Albrecht.[6] When dissolved in alkaline solution (n/10 NaOH), this compound gives a brilliant luminescence on oxidation with hypochlorites, ferricyanides, permanganates, persulphates, Cl, Br and I,

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[*] Contribution from the Physiological Laboratory, Princeton University.

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[6] Albrecht: Z. physik. Chem., **136**, 321 (1928). The material used in these experiments was kindly supplied by Dr. Albrecht, to whom I express my sincere thanks.

and H_2O_2, especially if there are present also substances decomposing H_2O_2, including peroxidases and blood. Such an alkaline solution of aminophthalichydrazid will be referred to as hydrazid solution.

Luminescence does not appear if pure oxygen is bubbled through the solution but a brilliant luminescence surrounds each bubble of ozone which is passed through the alkaline hydrazid.

One should therefore expect to find luminescence at an anode during electrolysis of hydrazid, free of halogens, and this is fully borne out by experiment. With good stirring of the solution a bright light appears at 2.8 volts and .0005 amperes which will last for some time. If the solution is not stirred a bright flash that dims quickly appears at 2.8 volts and a good steady luminescence at 0.5 volts, undoubtedly due to oxidation of hydrazid by the film of active oxygen. I plan making some efficiency studies at a later date.

Perhaps the most interesting luminescence is that which appears if freshly cut metals such as Al, Zn, Cd, and Sn are placed in the solution of hydrazid in *n/10* NaOH. No light was observed with Fe, Ni, Pb, Cu, Ag, Cr, Mn, Bi, As, Hg, Au, or Pt. It is especially bright if the metals are lifted out of the hydrazid solution to the air and also especially bright if amalgamated Al is used, when a continuous stream of H_2 is liberated and a precipitate of $Al(OH)_3$ forms. The question at once arises as to the cause of luminescence, at these metallic surfaces. It is known that hydrogen is formed from water by these metals. One might consider that the energy came from: (1) recombination of hydrogen atoms to molecules; (2) adsorption of hydrazid on metal or on $Al(OH)_3$ surfaces; (3) reaction of hydrazid with Na aluminate, zincate, or stannate; (4) formation of H_2O or H_2O_2 from H_2 and dissolved O_2.

That the first possibility is not the case is shown by the fact that no luminescence appears at most cathodes (note exception to be described later) where hydrogen is actively freed by electrolysis, and also by the fact that hydrogen in contact with platinized asbestos, or palladinized Pd in Na hypophosphite solutions (which liberates H_2), or Mg dissolving in NH_4 salts (which also liberates H_2) shows no luminescence when hydrazid is also present.

The second possibility is ruled out by the fact that $Al(OH)_3$, precipitated from $AlCl_3$ or NH_4 alum, mixed with hydrazid solution gives no luminescence,[1] and the third possibility is also ruled out by the fact that Al, Zn, Cd, and Sn boiled with n/10 NaOH, the supernatant liquid decanted and mixed with hydrazid gives no luminescence. The zincates, etc., should be formed under these conditions.

Regarding the fourth possibility, it is well known since the observation of Traube[2] (cf. Burdick[3] and Smith[4]) that H_2O_2 is formed at moist Zn sur-

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[1] A flash of luminescence will occur when hydrazid dissolved in alkali is made acid and also when this acid solution is again made alkaline, so that care must be taken to suspend the $Al(OH)_3$ in alkaline solution.

[2] Traube: Ber., 26, 1471 (1893).

[3] Burdick: J. Am. Chem. Soc., 48, 1179 (1926).

[4] Smith: J. Chem. Soc., 89, 481 (1906).

faces in contact with air. Dunstan, Jowett and Goulding[1] obtained the titanic acid test for H_2O_2 when Zn, Hg, Cu, Pb, Bi, Sn, and Ag (trace) are treated with slightly acid water containing oxygen, but none with Fe, and Barnes and Shearer[2] observed potentials at Al and Zn surfaces connected with H_2O_2 formation, but not with Cu, Pt, or Fe surfaces. There is therefore considerable evidence that under certain conditions H_2O_2 is formed at metal surfaces in presence of dissolved oxygen and I believe the hydrazid luminescence at these surfaces is due to its oxidation by H_2O_2.

H_2O_2 should also be formed at cathodes during electrolysis and should be most apparent with those metals possessing the greatest hydrogen overvoltage (since those metals have the least catalytic effect in causing recombination of H atoms, active in H_2O_2 formation).

Mercury has a high hydrogen overvoltage and should show luminescence when covered with a layer of aerated hydrazid in n/10 NaOH and made a cathode. Such is the case. The anode is a point, a fine Pt wire, so that the bright luminescence occurring at the anode will not interfere with observation of the weak luminescence due to H_2O_2, that actually appears over the cathode Hg surface under these conditions. When the current is reversed and Hg made an anode we can of course obtain the bright luminescence connected with nascent oxygen.

Other observations show that luminescence of hydrazid occurs under conditions when we should expect active oxygen to appear.

Thus, a piece of phosphorus placed in a layer of hydrazid solution so as to be half covered shows the bluish luminescence of oxidizing hydrazid due to ozone formation at the P surface, in addition to the greenish luminescence of the P itself undergoing oxidation.

H_2O_2 has been observed in oxyhydrogen and oxy-CO flames[3] and it is interesting to find a beautiful blue luminescence at the surface of hydrazid solutions when an oxy-gas or air-gas flame is directed on the surface. No such luminescence is observed at the surface of water or n/10 NaOH solution.

Finally it should be asked why it is not possible to observe oxidation of hydrazid and luminescence at platinized asbestos surfaces in contact with air or pure oxygen. As a matter of fact no luminescence appears when hydrazid is poured on Pt asbestos[4] (several samples were tried) and pure O_2 is bubbled through the solution. It is possible that the Pt surface is quickly poisoned by the hydrazid but there is little value in speculation in the absence of experimental data.

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[1] Dunstan, Jowett and Goulding: J. Chem. Soc., 87, 1548 (1905).

[2] Barnes and Shearer: J. Phys. Chem., 12, 155, 468 (1908).

[3] Traube: Ber., 26, 1471 (1893).

[4] Sometimes a faint flash of luminescence appears when hydrazid solution is poured on cotton, asbestos fiber, and other finely divided substances.

Summary

Luminescence of aminophthalichydrazid in dilute alkali occurs at any anode during the passage of current and at a cathode of Hg, at moist alkaline Al, Zn, Cd, and Sn metal surfaces, and when oxy-gas flames are played on the surface of the alkaline solution. This luminescence is due to active oxygen. Luminescence of hydrazid also occurs in contact with oxidizing phosphorus and is connected with ozone formation and decomposition. This hydrazid is suggested as a test for active oxygen. A mixture of oxy-luciferin and luciferase may be used as a test for active hydrogen. It is suggested that the term galvano-luminescence be used for luminescences associated with the passage of electric current through liquids.

EFFECT OF SOME FACTORS ON THE RING METHOD FOR DETERMINING SURFACE TENSION*

BY A. H. NIETZ AND R. H. LAMBERT

In connection with work carried out by one of us[1] on orientation at solid surfaces it became necessary to adopt a convenient and rapid method for determining surface tension. Further, work by Sheppard and Lambert[2] on flocculation and deflocculation of silver halides gave rise directly to an interest in the ring method. Certain phases of the method were therefore investigated, in particular the dependence of the ring method on contact angle, or degree of wetting of the ring by the liquid to be measured. The effect of certain physical factors such as the size of wire, dimensions of the ring, *etc.*, were briefly reviewed. This present paper is, however, in no sense a comprehensive study of the method, the effects of ring size having been given more exact treatment by MacDougall,[3] Harkins,[4] Johlin,[5] and others.

A convenient apparatus for the practical use of the ring method has been described by du Noüy[6] and is manufactured by the Central Scientific Company. This is the instrument used by us. The modified technic of Klopsteg[7] was employed throughout, as this seems without doubt correct. According to this, the liquid is lowered by a fine micrometer screw and the arm holding the ring is always kept at the zero of torsion of the tensiometer wire. Various tensiometer wires were used, and the wires giving the most convenient readings with the highest accuracy were chosen. Such a wire will give relatively high readings, *e.g.*, from 150° to 170°, when the ring leaves the surface of the liquid. Obviously it is not convenient to change wires always to obtain such high readings. Each wire was calibrated in dynes per degree by means of a small pan and weights substituted for the ring. In most cases in the following, however, the value used is that of the pull on the ring in degrees, designated as P.

The equation often applied to the tensiometer is

$$T = \frac{F}{2l}$$

where T is surface tension, F is the force in dynes required to pull out the ring ($F = kP$), and l is the average perimeter of the ring. It has, of course,

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* Communication No. 379 from the Kodak Research Laboratories, read at the Regional Meeting of the American Chemical Society, at Syracuse, N. Y., October 19, 1928.

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[2] Colloid Symposium Monograph, 4, 281-301 (1926).

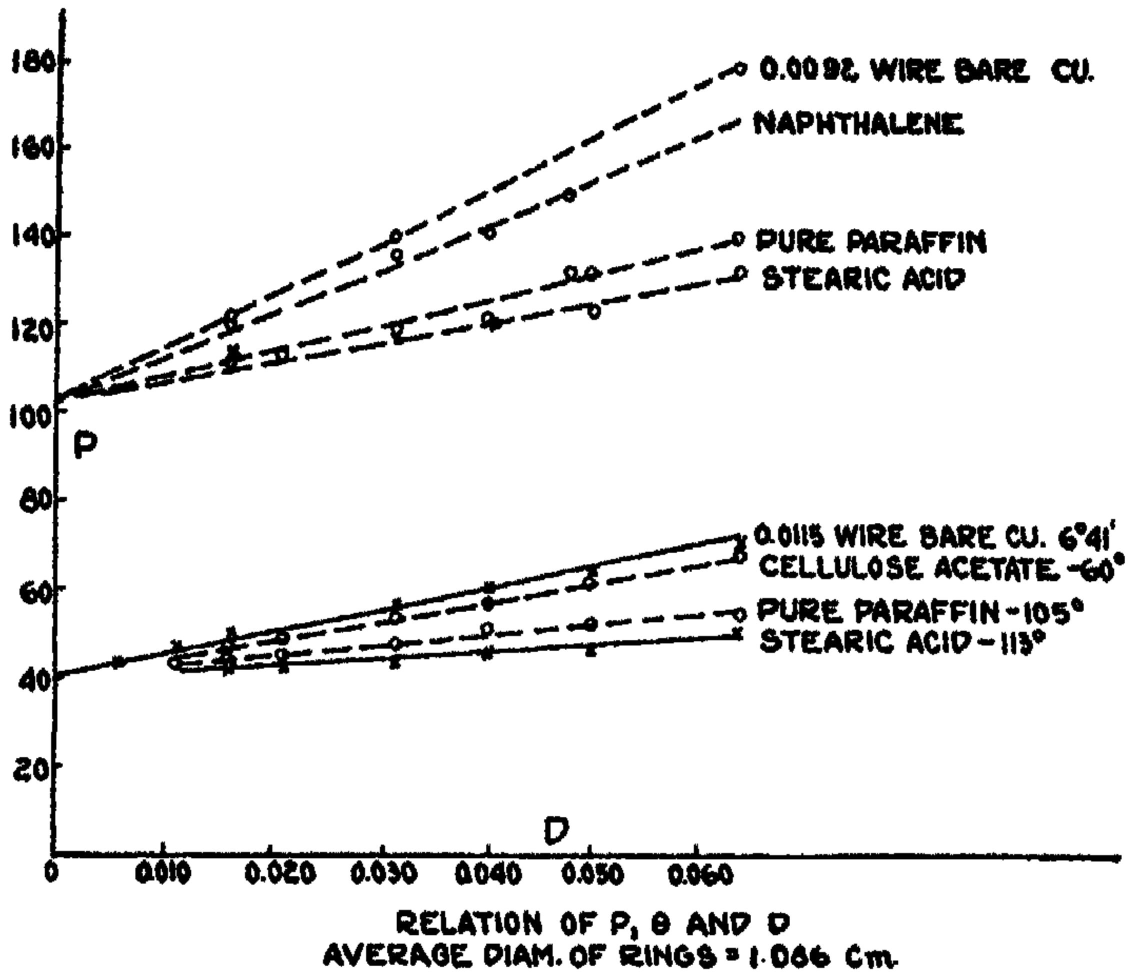
[3] Science, 62, 291 (1925).

[4] Science, 64, 333 (1926).

[5] Science, 64, 93 (1926).

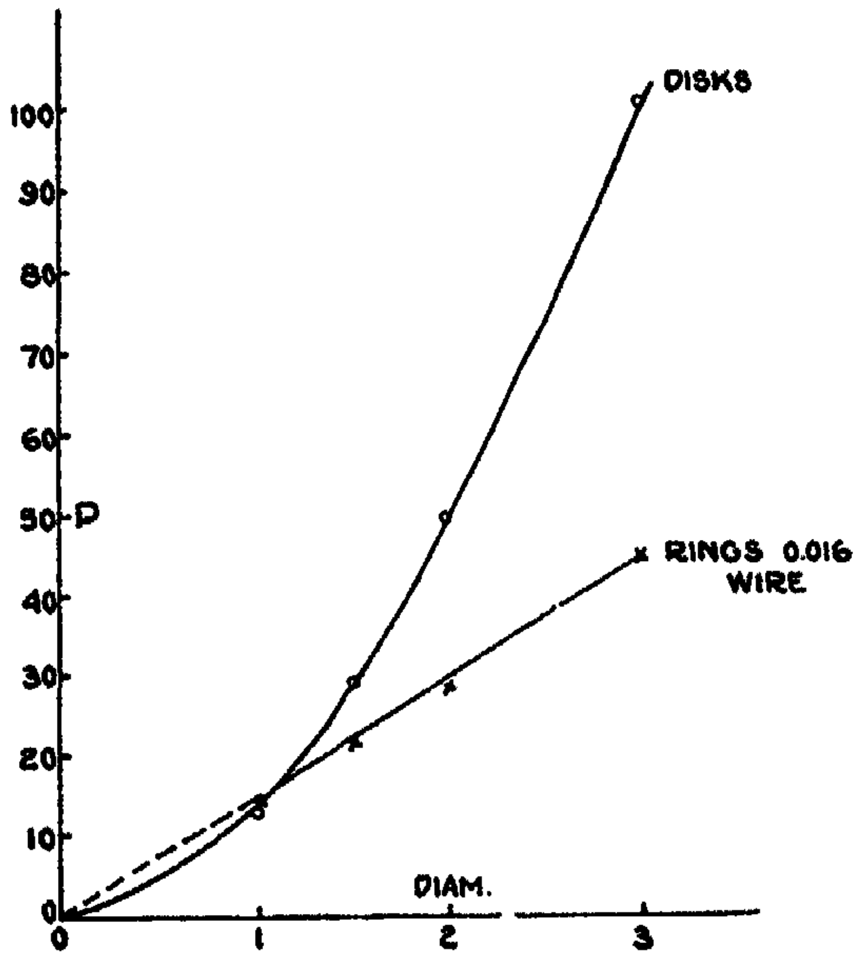
[6] J. Gen. Physiol., 1, 521 (1919).

[7] Science, 60, 319 (1924).



RELATION OF P, θ AND D
AVERAGE DIAM. OF RINGS = 1.066 Cm.

Fig. 1



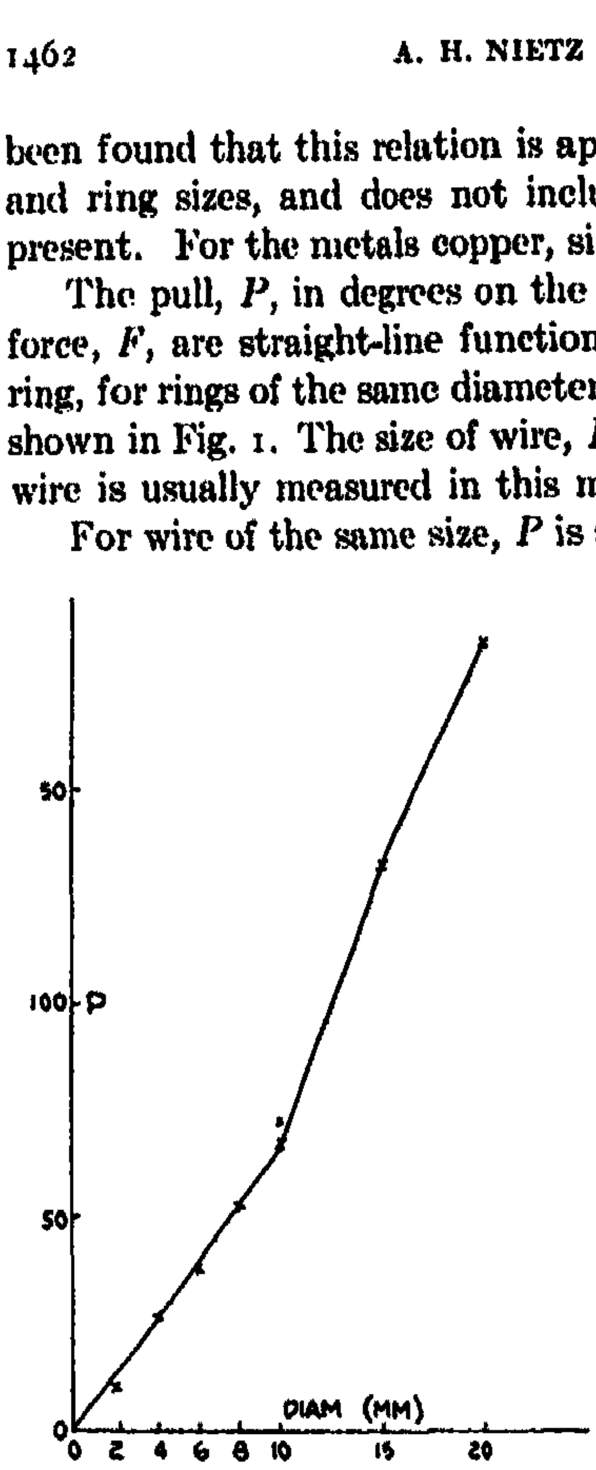
EFFECT OF SIZE (DIAM.)

Fig. 2

been found that this relation is applicable over only a narrow range of wire and ring sizes, and does not include the effect of contact angle which is present. For the metals copper, silver, and platinum, the latter is negligible.

The pull, *P*, in degrees on the dial of the tensiometer, and therefore the force, *F*, are straight-line functions of the size of wire, D, constituting the ring, for rings of the same diameter. Some of many such curves obtained are shown in Fig. 1. The size of wire, *D*, is given in inches for the diameter, since wire is usually measured in this manner.

For wire of the same size, *P* is also a straight-line function of the diameter of the ring, as shown in the lower curve of Fig. 2. MacDougall[8] has pointed out that for any sort of accuracy in absolute values, the ring should be larger than 1.5 cm. in diameter. Fig. 2 also includes results with disks of varying diameter. Disks, however, present complex problems in themselves, so that they seem to offer little in the application to surface tension measurement. Spheres were also tried though not further investigated, and the relation for pull and size is shown in Fig. 3. This is evidently approximately a straight line, while with disks the function is exponential.



CHANGE IN SIZE OF SPHERES

FIG. 3

The factor to which most attention was paid, however, was the effect of contact angle. Our curiosity was aroused in this direction by a table (Table I) published by Ferguson[9] in which the ring method is definitely classed as being independent of contact angle. This is approximately true, as stated, when it is used under certain conditions, but it can be shown that the statement is by no means generally true.

Numerous sets of curves like Fig. 1 were obtained and from these observations, and interpolations made from them, the data summarized in Fig. 4 were assembled. It is evident at once from this set of curves that the higher the wetting power of the liquid (in this case water) for the material of the ring, the more rapid the change in pull, *P*, with change of wire size. Conversely, when the degree of wetting is low, as in the lower curve ($\theta = 120°$) there is practically no change in pull with wire size.

If now we confine ourselves to one wire size, something further can be learned about the effect of contact angle. For this purpose a wire size, *D* of 0.064 in. was chosen. This will give data corresponding to a cross-section of

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[8] *Loc. cit.*

[9] Trans. Faraday Soc., **17**, 370 (1921).

TABLE I

Methods for measuring Surface Tension

- (A) Independent of contact-angle
  - Vibrations
    - (1) Vibrations of drop
    - (2) Waves on jet
    - (3) Ripples
  - Balance methods
    - (4) Pull on ring
    - (5) Tension in film
  - Bubbles and drops
    - (6) Pressure in pendent drop
    - (7) Large bubbles and drops
    - (8) Bubbles and drops (any size)
  - Capillary tubes
    - (9) Sentis' method
    - (10) Jaeger's method
- (B) Dependent on contact-angle
  - Capillary rise
    - (11) Capillary tube
    - (12) Capillary plates:
      - (*a*) parallel
      - (*b*) inclined
    - (13) Single plate
    - (14) Large cylinders
  - Balance methods
    - (15) Wilhelmy's method
    - (16) Pull on sphere
    - (16) Pull on sphere
    - (17) Pull on disk
    - (18) Buoyancy method
  - Bubbles and drops
    - (19) Total depth of large bubbles and drops

(20) (Unclassified) Drop-weight method.

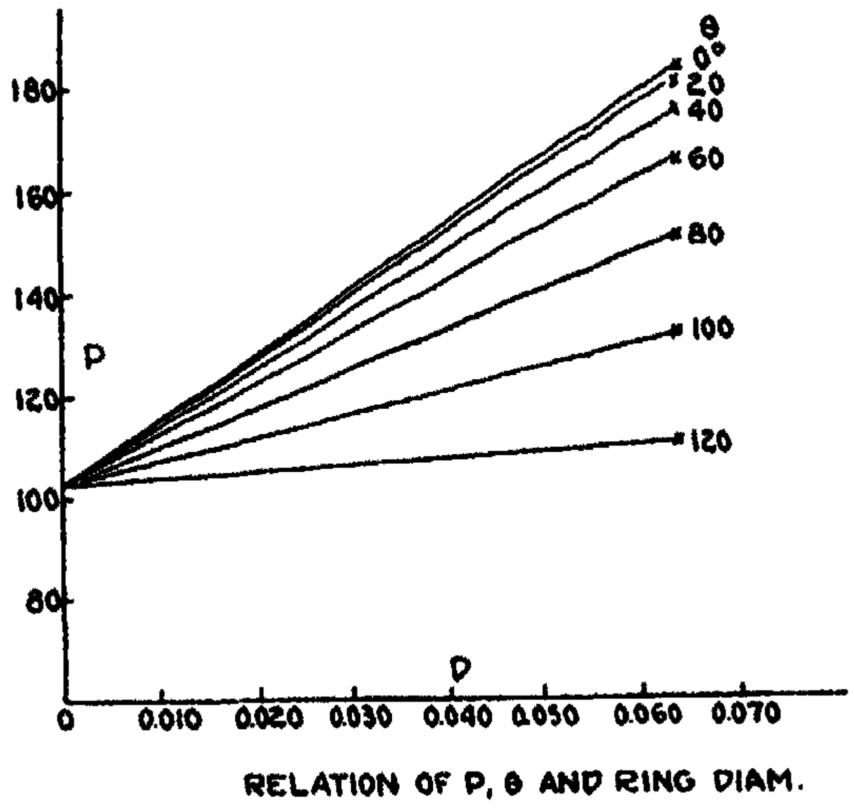


Fig. 4

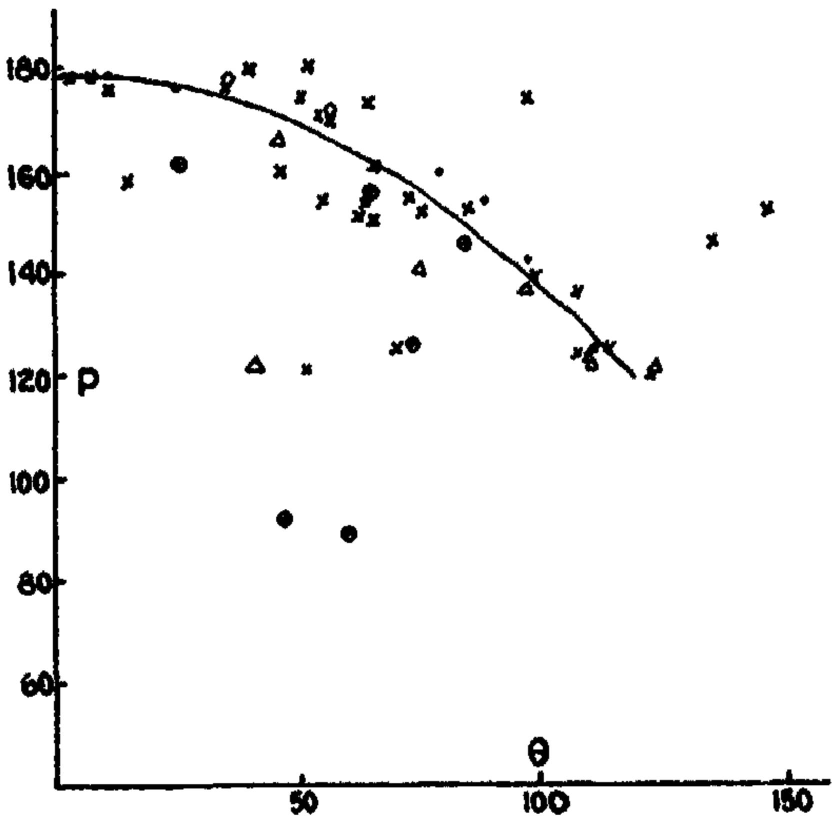
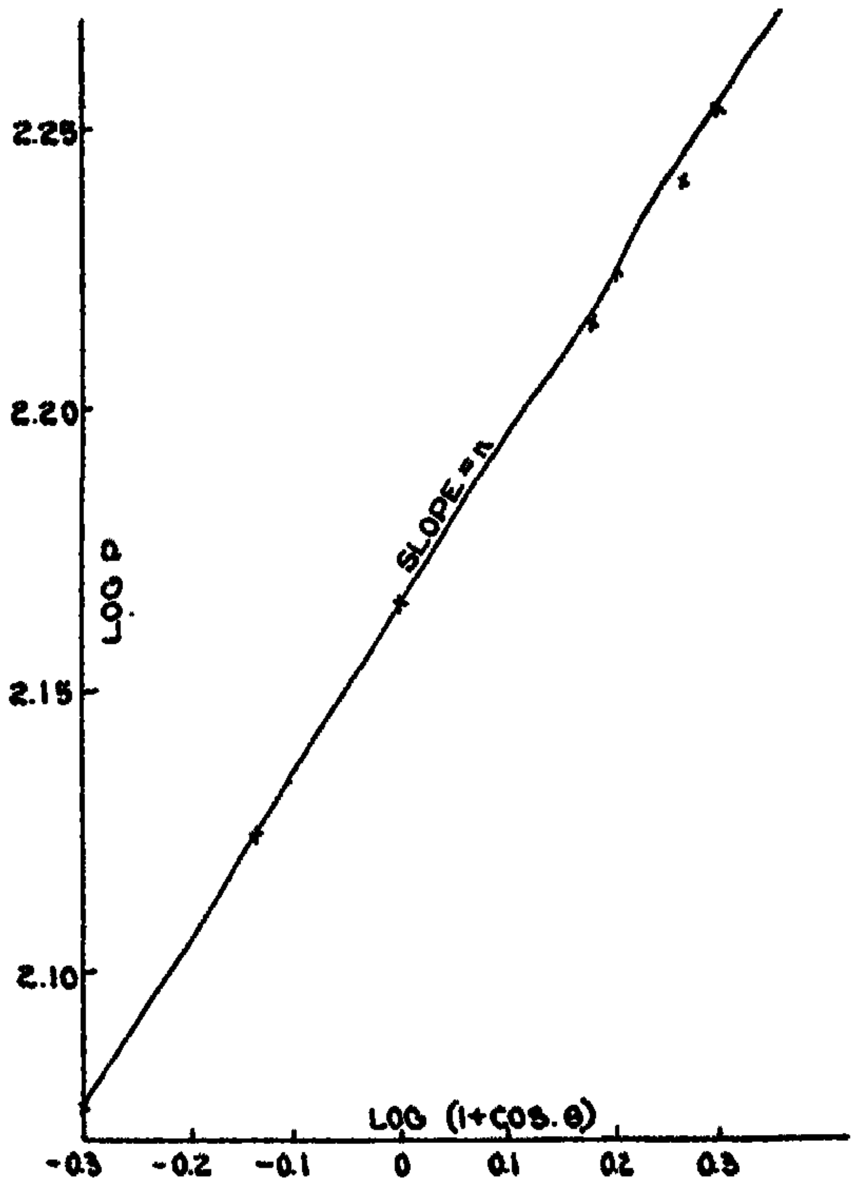


Fig. 5
Effect of Contact Angle on Pull of the Tensiometer Ring.

the curves in Fig. 4 taken at $D = 0.064$. Actual observations made under these conditions are shown in Fig. 5, where for a given wire size (0.064 in.) the pull P is plotted against the angle θ independently determined. The ring was dipped into a small quantity of the molten solid, the coating being as thin as possible. The solids used covered a wide range of organic substances such as hydrocarbons, alcohols, aldehydes, ketones, acids, *etc.* There are, of course, several sources of error and factors causing discrepancies involved in this procedure.



DETERMINING FUNCTION FROM CURVE

Fig. 6

In the first place there is a variation in the actual ring size, D, resulting from variation in the thickness of the coating. Further, it was shown in a previous paper[10] that conditions during crystallization may have a large effect on surface orientation, so no doubt there are variations in the surface from this cause. In spite of the very erratic and scattered appearance of these observations they show an almost certain correlation on mathematical treatment. A Bravais-Pearson correlation coefficient was calculated for some 75 pairs of observations, this coefficient being so high as to indicate

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[10] J. Phys. Chem., 32, 268 (1928).

a practically certain relation between pull and contact angle. For all observations this coefficient was 3.73, and when the most erratic results were excluded, 9.78.

Having determined that there is a definite relation between P and θ, we next attempted to set up the form of the function. It was assumed that the term $(1 + \cos\theta)$ might enter in the expression and accordingly log P was plotted against $\log(1 + \cos\theta)$. This proved a straight line as shown in Fig. 6. Substituting F for kP this gives rise to the expression

$$\mathrm{F} = 2\mathrm{lT}(1 + \cos\theta)^{\mathrm{n}}$$

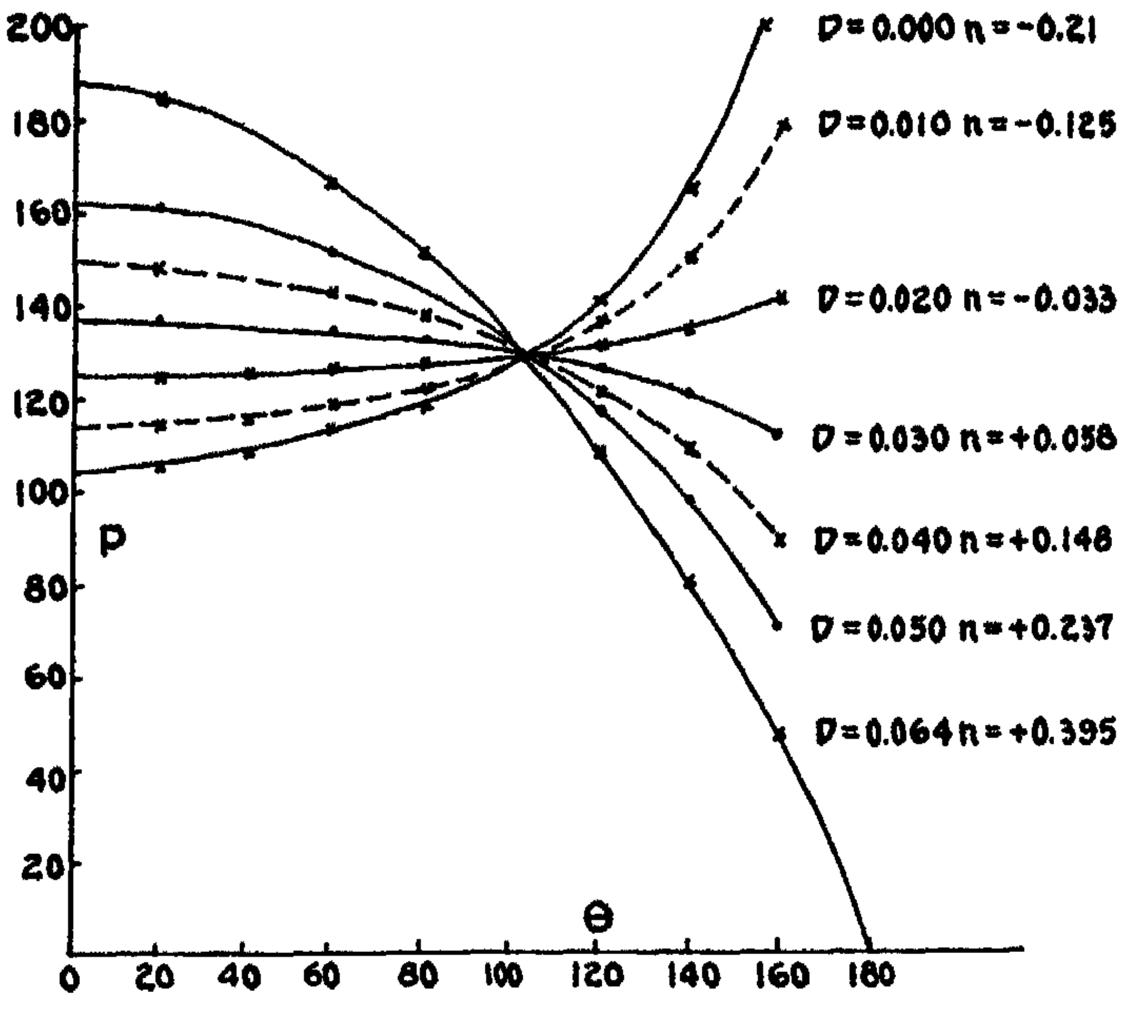

Fig. 7

where l is the perimeter of the ring, and the other symbols have the meanings previously given. The factor l enters as P is in dynes and T in dynes per cm. By further treatment of observed data n is found to be related as follows

$$\mathrm{n} = \mathrm{k}\frac{\mathrm{D}}{\mathrm{l}} - \mathrm{k}_1$$

and for the case under examination, where $D = 0.064$

$$\mathrm{n} = 13.1\,\frac{\mathrm{D}}{\mathrm{l}} = 0.227.$$

That this expression for the relation between F and θ, $\mathrm{F} = 2\mathrm{lT}(1 + \cos\theta)^{\mathrm{n}}$, holds only when D is relatively large is evident at once from Fig. 7, which represents a family of curves calculated from the equation. When D is somewhat less than 0.030, n becomes negative, and for negative values of n the curves turn upward beyond about $\theta = 105°$. This is, of course, absurd, as it is inconceivable that the pull should increase with lower wetting power.

From Fig. 7 it is also clear that at some size of wire in the neighborhood of $D = 0.020$ the pull will be independent of the contact angle. This may be true and may be the reason why it has been thought that P and θ are not related. Further, at about the angle of paraffin, 105 to 110°, Fig. 7 shows a point where the pull is approximately independent of the wire size. The latter was not borne out by the experimental data for paraffin (see Fig. 1) and would be extremely difficult to prove or disprove experimentally owing to the physical difficulties involved in coating organic substances evenly to a definite thickness and to uncontrolled factors affecting the nature of the solid surface.

We did not succeed, in the limited time given to the problem, in developing a relationship which would hold over a wider range. The equation given did fit the data, however, very nicely for the size of wire used, and the curve put through the observations of Fig. 5 is the result of least-square calculations based on the equation. From Fig. 1 it is evident that since we have straight lines of the type shown, we must also have the relation

$$F = mD + b.$$

Accordingly, if we are right, this should be compatible with $F = 2lT(1+\cos\theta)^n$, where $n = 13.1D/l = 0.227$, which was found to be the case.

Summary

1. The ring method for surface tension measurement was investigated as to the effect of dimensions of the ring and as to the effect of contact angle.

2. It was definitely proved that there is a relation between the pull on the ring and the angle of contact between the material of the ring and the liquid.

3. The form of the function showing this relationship was found to be

$$F = 2lT\,(1 + \cos\theta)^n$$

though this did not hold over the entire range of wire sizes.

4. The classification of the ring method as being free from the effect of contact angle is definitely in error, being probably partly caused by an accidental choice of rings and materials which showed little if any effect.

Rochester, N. Y.,
April 1, 1929.

THE APPLICATION OF DIFFERENTIAL POTENTIOMETRIC TITRATION TO THE ESTIMATION OF WEAK ACIDS IN DILUTE SOLUTION*

BY BEVERLY L. CLARKE AND LELAND A. WOOTEN

Introduction

In connection with work on the acetic acid content of woods which arose from an investigation of the corrosion of lead cable sheath in creosoted wood ducts[1] it became necessary to estimate with precision acidities of water extracts of woods which were of the order of several ten-thousandths normal in acetic and formic acids. The frequent presence of wood pigments (which were in some cases natural indicators) and the high degree of dilution rendered inapplicable methods of titration involving indicators. For the same reasons, and also because of the precision desired, a number of electrometric methods were eliminated after trial. The differential electrometric method in the form developed by MacInnes[2] showed the greatest promise. In order to adapt the differential method to the requirements of our special problem of the estimation of weak acids in very low concentrations, certain modifications in the method and a new form of apparatus were developed. A somewhat similar electrode has recently been suggested by Erich Müller.[3]

The apparatus is illustrated in Fig. *1*. The procedure for making a titration is as follows: Gas is passed through the capillary tube C until the air in the solution has been displaced and the potential difference between the electrodes C and D, on closing A and sucking up solution into C by compressing and dilating B, has reached a small constant value E_0 (zero in the ideal case). With the gas cut off and C filled with solution, a small increment ΔB of the base solution is added from the burette to the solution about D, the diffusion of which into C is minimized by the fine capillary at the base of C. The concentration cell thus set up shows an electromotive force E. As ΔB is made smaller $E-E_0/\Delta B$ (or $\Delta E/\Delta B$) approaches dE/dB and a plot of $\Delta E/\Delta B$ against B approximates the differential of the usual E/B curve. The end-point is estimated from such data by methods to be described in the theoretical section.

Theoretical

So far as is known to us, the complete theory of titration by the differential method has not been worked out. We present a theory applicable to the solutions with which we are working.

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* Contribution from Bell Telephone Laboratories.

[1] Burns and Freed: J. Am. Inst. El. Eng., 47, 576 (1928).

[2] MacInnes: Z. physik. Chem., Cohen-Festband, 217 (1927).

[3] Müller: Z. physik. Chem., 135, 102 (1928).

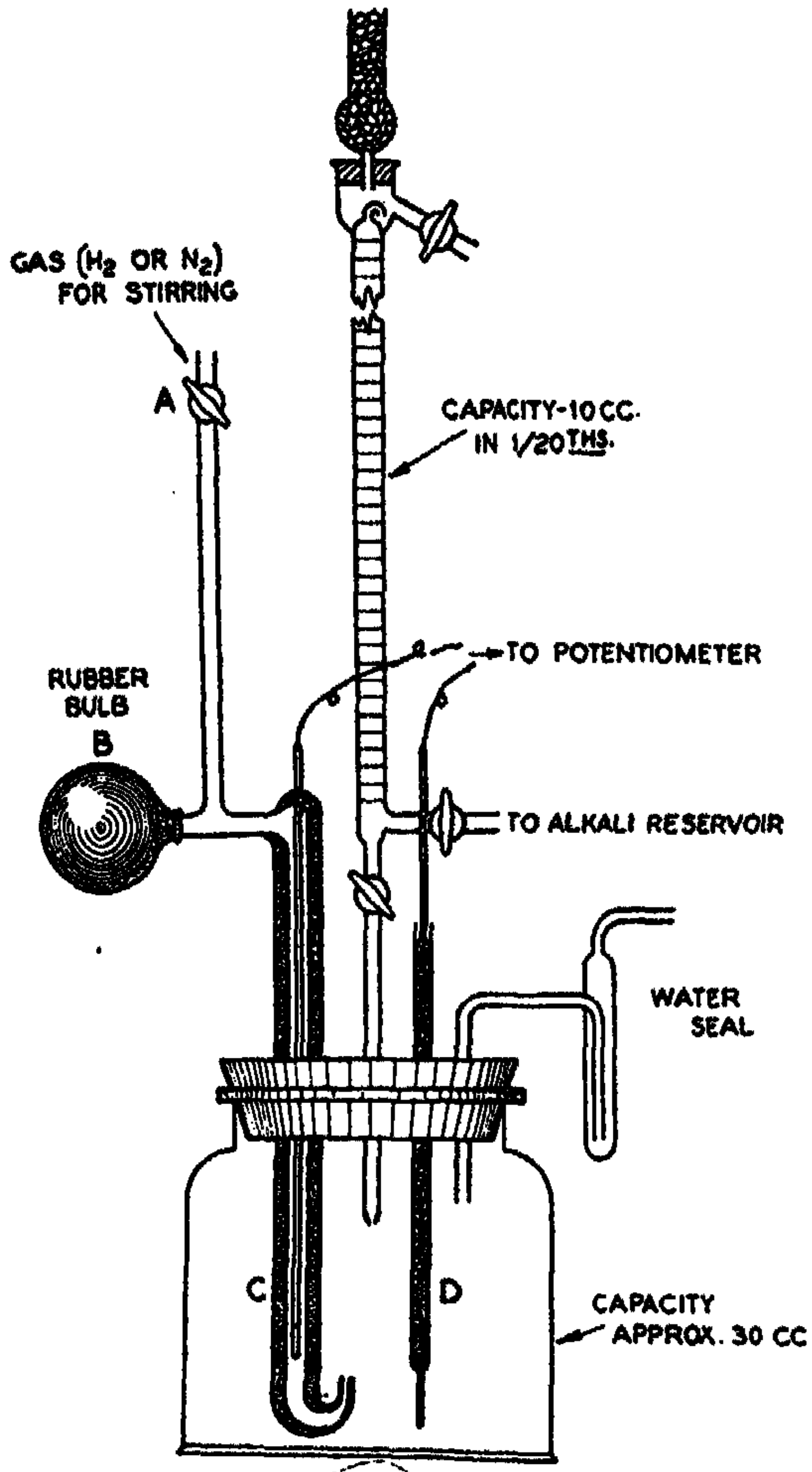

fig 8.608

FIG. 1

The differences of potential measured during a differential titration arise from hydrion concentration cells of continually varying hydrion ratios; and are expressible by the Nernst equation,

$$\Delta E = 0.059 \log \frac{[H^+]_1}{[H^+]_2}, \qquad (1)$$

where the subscripts 1 and 2, here as in the sequel, refer to electrodes C and D respectively. (Cf. Fig. 1).

Consider a point during a titration at which the solution about each electrode is of the same composition. If we so choose the volume of the solution to be titrated that the volume of reagent required for neutralization is negligible in comparison, then the total volume may be assumed constant

Further, since the salt of the weak acid and the strong base is completely ionized, the concentration of cation present in the solution, i.e., $[B^+]_o$, is strictly proportional to the amount of alkali reagent which has been added.

Let an increment of alkali solution be added to the solution about D such that this solution is given the composition $[B^+]_o + \Delta\,[B^+]_o$, causing a difference of potential ΔE to be set up between D and C. It is desired, then, to plot $\frac{\Delta E}{\Delta [B^+]}$ against $[B^+]$. The particular value of $[B^+]$ to be used lies between $[B^+]_o$ and $([B^+]_o + \Delta[B^+]_o)$, and for practical purposes it is our procedure to take the middle point, or to assume that $[B^+] = [B^+]_o + 1/2\ \Delta[B^+]_o$. This is equivalent to assuming that E and $[B^+]$ are linearly related between $[B^+]^\circ$ and $([B^+]_o + \Delta[B^+]_o)$ or that, between these limits,

$$\frac{d^2E}{d[B^+]^2} = 0.$$

The validity of this assumption depends, of course, on the use of small values of $\Delta[B^+]$; near the end-point, where the rate of increase of E with $[B^+]$ approaches infinity, the error introduced vanished.

In the theory of the titration of a weak acid with a strong base the following approximation equation[1] has been developed:

$$[H^+] = K_a \frac{[S] - [B^+]}{[B^+]} = K_a \frac{1 - \frac{[B^+]}{[S]}}{\frac{[B^+]}{[S]}}, \tag{2}$$

where K_a is the dissociation constant of the weak acid and [S] the concentration of acid present in the solution before the titration.

For simplicity in notation let a quantity F, the fraction of the acid neutralized, be defined by

$$F = \frac{[B^+]}{[S]}. \tag{3}$$

The general equation (2) then becomes,

$$[H^+] = K_a \frac{1 - F}{F}. \tag{4}$$

For the solution surrounding electrode C,

$$[H^+]_1 = K_a \frac{1 - \frac{[B^+] - 1/2\ \Delta[B^+]}{[S]}}{\frac{[B^+] - 1/2\ \Delta[B^+]}{[S]}}.$$

Since [S] is constant, from equation (3)

$$\Delta F = \Delta \frac{[B^+]}{[S]}. \tag{5}$$

Therefore,

$$[H^+]_1 = K_a \frac{1 - F + 1/2\ \Delta F}{F - 1/2\ \Delta F}; \tag{6}$$

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[1] Clark: "The Determination of Hydrogen Ions," 22 (1928).

and for the bulk of the solution, that about electrode D,

$$[H^+]_2 = K_a \frac{1 - \frac{[B^+] + 1/2\ \Delta[B^+]}{[S]}}{\frac{[B^+] + 1/2\ \Delta[B^+]}{[S]}}$$

$$= K_a \frac{1 - F - 1/2\ \Delta F}{F + 1/2\ \Delta F}. \qquad (7)$$

Substituting equations (6) and (7) in equation (1) we have:

$$\Delta E = E - E_0 = 0.059 \log \frac{(1 - F + 1/2\ \Delta F)\ (F + 1/2\ \Delta F)}{(1 - F - 1/2\ \Delta F)\ (F - 1/2\ \Delta F)}, \qquad (8)$$

which describes the course of the differential curve up to the equivalence point.

As alkali is added to the right of the equivalence point (i.e., when $F > 1$) the curve is an approximation to the differential of the dilution curve of a strong base, provided that we neglect hydrolysis. In a later section we shall show the justification for neglecting hydrolysis.

For a strong base,

$$[OH^-] = [B^+] - [S] = (F - 1)\,[S].$$

$$\therefore \qquad [H^+] = \frac{k_w}{(F - 1)\,[S]}. \qquad (9)$$

As in the derivation of the acid curve,

$$[H^+]_1 = \frac{k_w}{(F - 1/2\ \Delta F - 1)\,[S]}, \qquad (10)$$

and

$$[H^+]_2 = \frac{k_w}{(F + 1/2\ \Delta F - 1)\,[S]}. \qquad (11)$$

Substituting equations (10) and (11) in equation (1) we obtain the equation for the differential curve on the alkaline side of the end-point:

$$\Delta E = 0.059 \log \frac{F + 1/2\ \Delta F - 1}{F - 1/2\ \Delta F - 1}. \qquad (12)$$

In Fig. 2, a theoretical titration curve is plotted from equations (8) and (12), and experimental points are shown for comparison.

It is manifest that the value of ΔF, i.e., the size of the increment of base added to produce ΔE, affects the shape of the titration curve, and it will be helpful to show this effect graphically. The curves in Fig. 3, differing only in the values of ΔF, indicate that the end-point is sharper as ΔF is decreased. At the same time the actual value in millivolts of ΔE at measurable distance from the end-point also decreases; so that a lower limit to ΔF is set by the accuracy with which ΔE can be measured. We find experimentally that this limit for the titration of 0.001 N HAc is at about $\Delta F = 0.01$.

Estimation of End-point:

Rearranging equation (8), we obtain

$$[S] = \frac{[B^+]^2 - 1/4\ \Delta[B^+]^2}{[B^+] - 1/2\ \Delta[B^+]\dfrac{(\gamma + 1)}{(\gamma - 1)}}, \qquad (13)$$

where $\gamma = \log^{-1}(\Delta E/59)$, with ΔE in millivolts. Equation (13) allows one to compute a value for $[S]$ (which is the end-point) from one measurement of ΔE for a given $[B^+]$ on the acid side. The corresponding formula from the equation for the alkaline curve would be less accurate because of disturbances on the alkaline side caused by quinhydrone.

Two other methods are suggested for estimating the end-point. Let equation (8) be rewritten:

$$\Delta E = 0.059 \log \frac{([S] - [B^+] + 1/2\ \Delta[B^+])\ ([B^+] + 1/2\ \Delta[B^+])}{([S] - [B^+] - 1/2\ \Delta[B^+])\ ([B^+] - 1/2\ \Delta[B^+])}. \qquad (14)$$

Now, the function represented by equation (14) becomes infinite at some point close to but slightly to the left of the equivalence point. It is evident, further, that the value of $[B^+]$ to which the function is asymptotic differs from the true end-point $[S]$ by an amount dependent upon the magnitude of $\Delta[B^+]$. To formulate the true equivalence point $[S]$ in terms of $[B^+]$ for the asymptote (which is estimated by extrapolation from experimental data) and of $\Delta[B^+]$ (which is known), we equate the righthand member of (14) to infinity, obtaining:

$$[S] = [B^+] + 1/2\ \Delta[B^+]. \qquad (15)$$

It is desirable that as many points as possible be taken since the accuracy of $[S]$ in equation (15) is largely conditioned by the accuracy with which $[B^+]$ for the asymptote can be read from the plot.

It is to be noted here that there is nearly always one point—that closest to the end-point—in every titration which does not fall smoothly on either the right or the left-hand curve. This is to be explained as follows: If we are so close to the end-point that the increment $\Delta[B^+]$ is more than sufficient to effect complete neutralization then the value of ΔE obtained will be the sum of two ΔE's, one determined by equation (8) and the other by equation (12). The measured ΔE will not, therefore, be perfectly expressed by either equation. An example is shown in Fig. 2 (point A). This anomalous point is, of course, to be disregarded when drawing smooth curves through the experimental points.

The third method is illustrated in Fig. 4. Smooth curves are drawn through the plotted experimental points (the circles). Assuming that the two curves are symmetrical, the true equivalence point lies, then, half-way between A and D. This method has an inherent error due to the departure from symmetricality of the curves, and to the uncertainty of the graphical extrapolation. Also, certain anomalies, probably referable to the quinhydrone, are exhibited on the alkaline side which render extrapolation exceedingly dangerous.

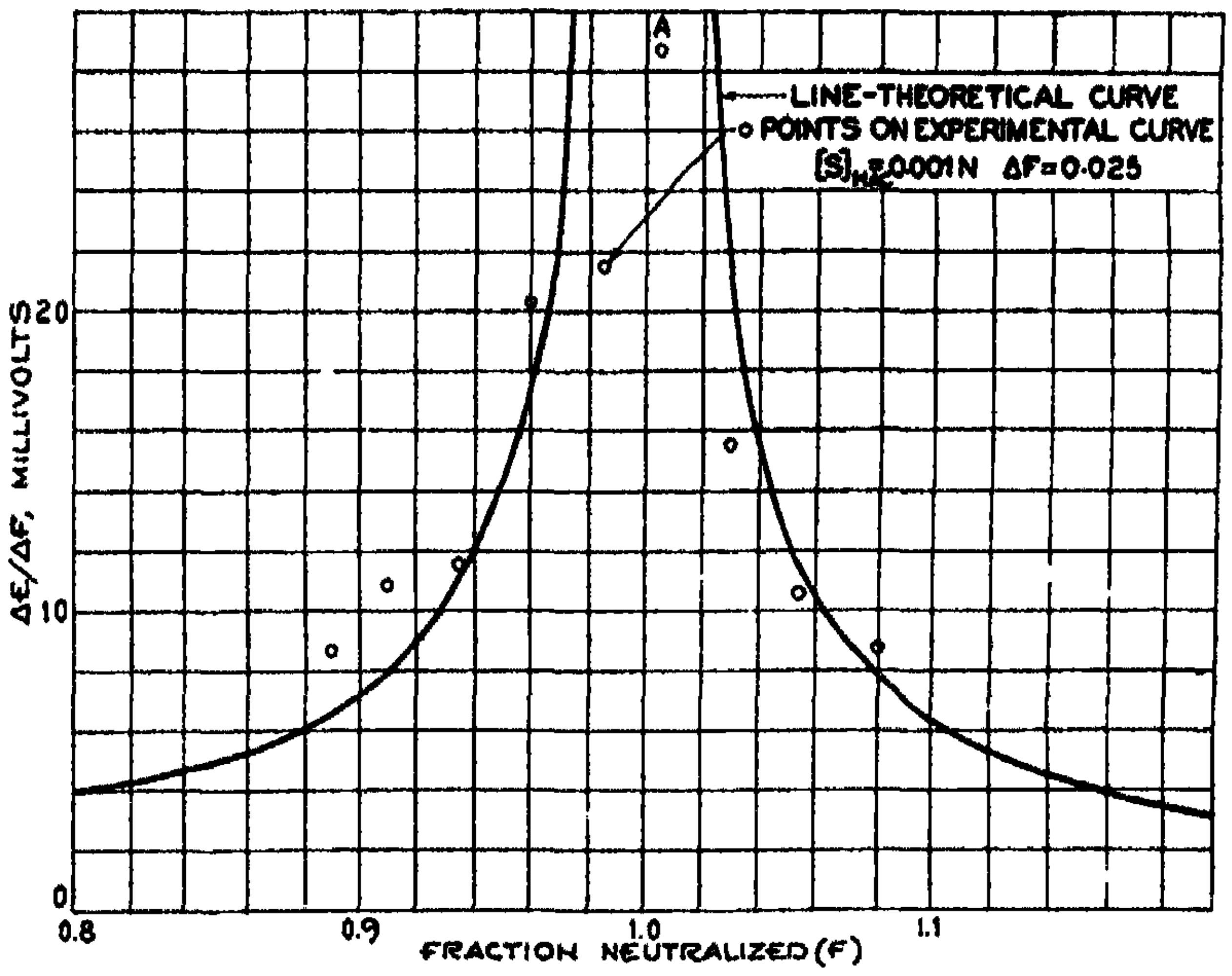
A
LINE-THEORETICAL CURVE
o POINTS ON EXPERIMENTAL CURVE
[S]HAc = 0.001N ΔF = 0.025
ΔE/ΔF, MILLIVOLTS
0
10
20
0.8
0.9
1.0
1.1
FRACTION NEUTRALIZED (F)

FIG. 2

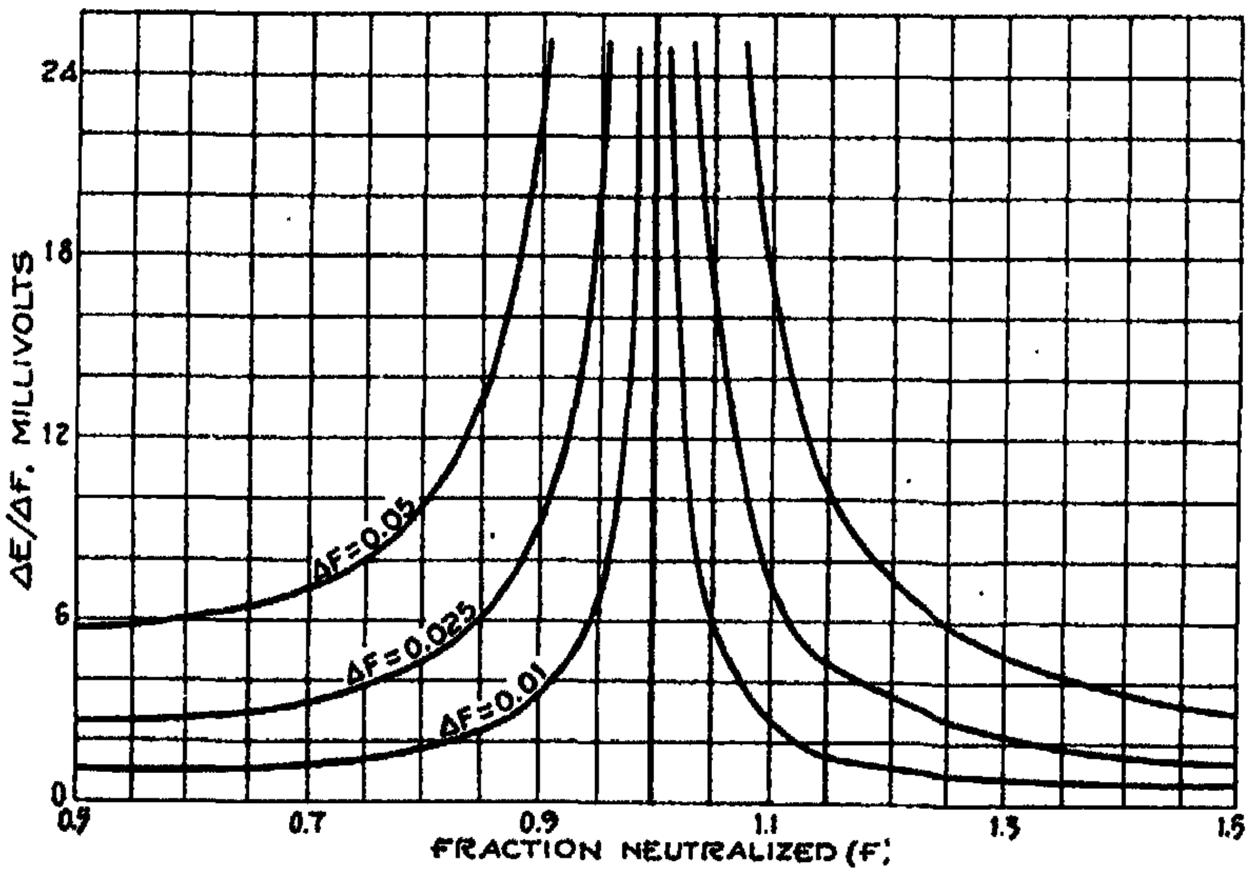
ΔF=0.05
ΔF=0.025
ΔF=0.01
ΔE/ΔF, MILLIVOLTS
0
6
12
18
24
0.5
0.7
0.9
1.1
1.3
1.5
FRACTION NEUTRALIZED (F)

FIG. 3

Experimental

With the purpose of discovering the concentration range through which this method is useful, titrations of various concentrations of acetic acid with barium hydroxide were made. We find that, whereas 0.0004 N acetic acid can be titrated with reasonable accuracy, weaker solutions are not susceptible of precise analysis. This, we consider, is owing to the limitations inherent in the method and in the type of solutions under consideration. A series of titrations of 0.0004 N HAc was then made in order to determine the reproducibility of the end-point at this dilution; and for comparison purposes a similar series on 0.001 NHAc was made.

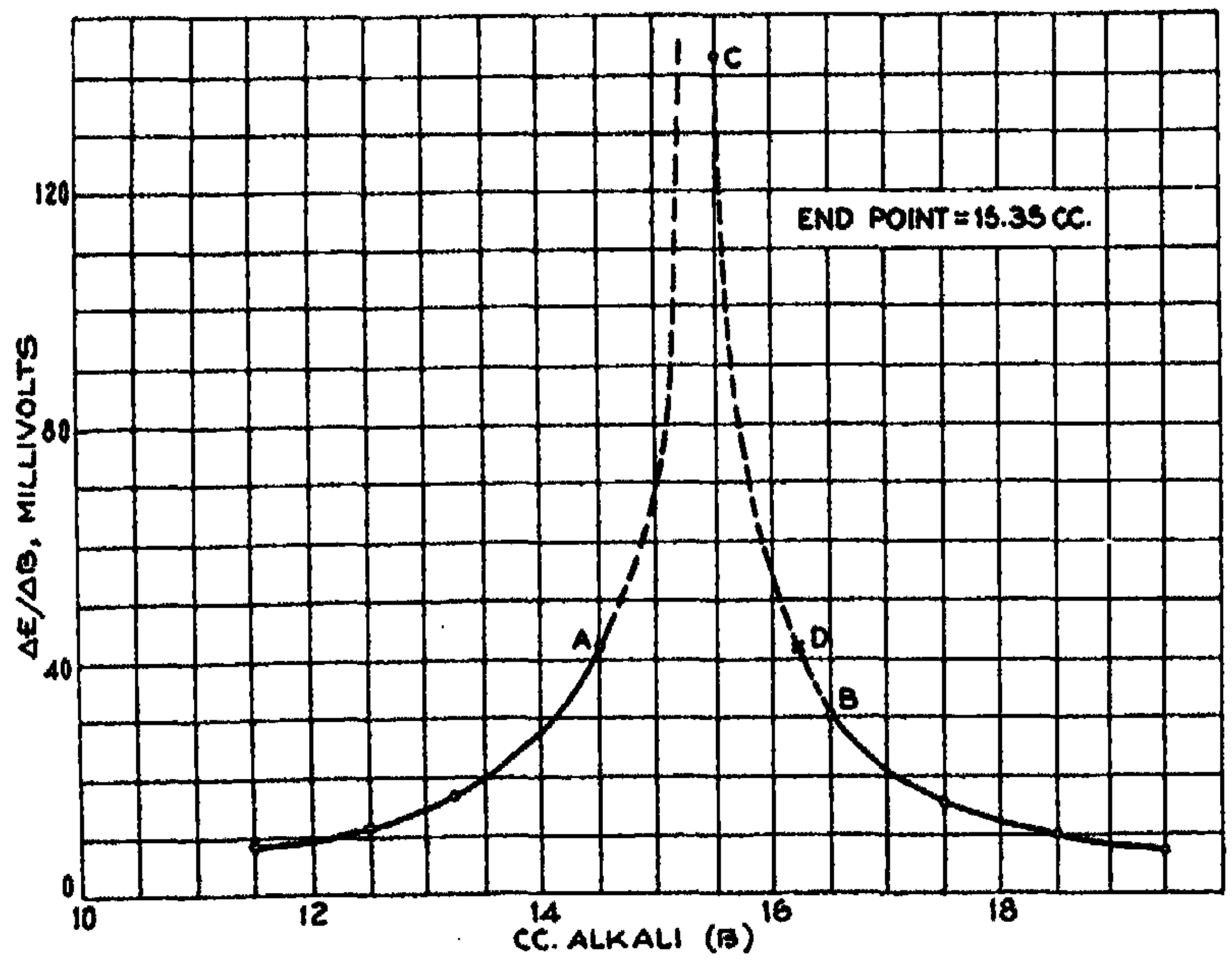

FIG. 4

The electrode system consisted of two bright platinum wires dipping into the unknown acid solution. Potassium chloride was added to make the solution conductive. The electrodes were cleaned between titrations by immersion in hot chromic acid mixture followed by treatment in hot sodium hydroxide solution to remove grease and traces of acid absorbed by the platinum. Prolonged washing in distilled water completed the cleaning process.

On the acid side of the equivalence point, equilibrium was attained very quickly (from 1 to 2 minutes) after the addition of an increment of alkali. On the alkaline side of the curve, however, the potentials were somewhat unsteady and showed a tendency to drift.

The titrations were conducted in a closed system in an atmosphere of nitrogen or hydrogen purified by passing through several towers of soda lime and through an electric furnace containing metallic copper at 300°C. Traces of oxygen caused the electrode potentials to drift and the results to be generally unsatisfactory.

The 0.001 N barium hydroxide used in all titrations was prepared by diluting with CO_2-free distilled water, a portion of a saturated solution of c.p. barium hydroxide. This solution was well protected from atmospheric carbon dioxide by a 3-foot length of soda lime tube, and was connected directly to the automatic burette by means of a syphon. The alkali was standardized frequently against standard hydrochloric acid by the differential method.

In order to stabilize the potentials the solutions were saturated with quinhydrone (Eastman). Potential differences were measured with a Leeds & Northrup Type K potentiometer.

Experimental Results

In Table I detailed data for a titration are given, while Table II summarizes the series of measurements on 0.001 N acid. The unit of potential difference is one millivolt. From Table III we see that the average deviation from the mean of a series of separately estimated end-points in the titration of 0.001 N HAc is ± 0.8%.

TABLE I

Titration of approx. 0.001 N HAc with 0.001 N $Ba(OH)_2$
Vol. of HAc = 20 cc.
Increment of alkali = 0.5 cc.

cc Alkali	E_0	E	ΔE
17.50	3.9	7.9	4.0
19.00	3.5	10.1	6.6
19.50	1.8	10.7	8.9
20.00	1.3	15.9	14.6
20.50	1.5	18.4	16.9
21.00	3.1	25.2	22.1
21.50	4.1	22.9	18.8
22.00	6.8	22.9	16.1
22.50	10.7	20.6	9.9
23.00	3.5	11.1	7.6

TABLE II

Titrations of approximately 0.001 N HAc

cc Alkali	Titration 2 ΔE	Titration 3 ΔE	Titration 4 ΔE	Titration 5 ΔE
17.50	4.6	3.8	3.6	—
18.00	5.6	4.6	4.4	5.8
18.50	5.8	5.2	6.2	5.7
19.00	6.8	6.2	7.1	8.2
19.50	9.0	8.9	8.6	9.9
20.00	12.6	12.6	9.2	12.2
20.50	16.8	17.2	11.8	15.9
21.00	24.6	20.3	16.8	23.6
21.50	18.9	24.6	24.1	22.2
22.00	16.8	16.2	18.1	16.1
22.50	9.9	15.1	17.3	16.2
23.00	8.2	9.2	10.1	11.8
23.50	—	—	6.2	9.2
24.00	—	—	5.8	9.4

TABLE III

Estimation of End-points

Titration No.	cc Alkali	Deviations
1	20.87	−0.06
2	20.80	−0.13
3	21.09	+0.16
4	21.18	+0.25
5	20.71	−0.22
Mean	20.93	±0.16

Tables IV and V present similar data for 0.0004 N HAc. From Table V the average deviation on these extremely dilute solutions is ± 1.7%.

TABLE IV

Titration of approx. 0.0004 N HAc with 0.001 N $Ba(OH)_2$
Vol. of acid = 25 cc.
Increment of alkali = 0.25 cc.

cc Alkali	Titration 1 ΔE	Titration 2 ΔE	Titration 3 ΔE
7.25	2.8	2.1	—
8.25	6.0	—	5.8
8.75	—	—	11.4
9.00	—	8.0	11.1
9.25	9.6	10.9	12.6
9.50	13.1	12.5	16.1
9.75	14.9	16.9	13.1
10.00	13.8	10.7	14.2
10.25	15.0	10.6	16.2
10.50	8.8	7.5	8.9
10.75	7.5	7.2	7.8
11.00	7.1	—	—
11.75	4.0	—	—

TABLE V

Estimation of Endpoints

Titration No.	cc Alkali	Deviations
1	9.7	+0.2
2	9.6	+0.1
3	9.3	−0.2
Mean	9.5	±0.17

Discussion

For the purpose of demonstrating the actual constancy of [S] in equations (13) and (15) and hence the validity of these equations for computing the equivalence point, data are presented in Table VI which are calculated from data in Tables I and II by equation (13).

From Table VI it is apparent that equation (13) holds surprisingly well in view of the fact that it is based on an approximatiom. Averaging the mean deviations we obtain ± 1.0%, which is the probable error in the endpoint computed from a single observation. If 8 or 10 observations are taken and averaged, the probability is high that [S] so computed will differ from

TABLE VI

[S] Computed by Equation (13) from data in Tables I and II

	Titration 1			Titration 2			Titration 3			Titration 4			Titration 5		
[B+] cc.	ΔE Milli-volts	[S] cc.	% deviation from mean	ΔE Milli-volts	[S] cc.	% deviation from mean	ΔE Milli-volts	[S] cc.	% deviation from mean	ΔE Milli-volts	[S] cc.	% deviation from mean	ΔE Milli-volts	[S] cc.	% deviation from mean
17.25	4.0	21.19	+1.51	4.6	20.57	−1.1	3.8	21.43	+1.6	3.6	21.73	+2.6	—	—	—
17.75	—	—	—	5.6	20.39	−2.0	4.6	21.06	−0.1	4.4	21.24	+0.3	5.8	20.28	−2.0
18.25	—	—	—	5.8	20.77	−0.1	5.2	21.10	+0.05	6.2	20.58	−2.8	5.7	20.83	+0.6
18.75	6.6	20.92	+0.23	6.8	20.85	+0.2	6.2	21.07	−0.1	7.1	20.82	−1.7	8.2	20.51	−1.0
19.25	8.9	20.82	−0.29	9.0	20.80	+0.0	8.9	20.81	−1.3	8.6	20.87	−1.5	9.9	20.65	−0.3
19.75	16.9	20.56	−1.49	12.6	20.83	+0.1	12.6	20.84	−1.2	9.2	21.27	+0.4	12.2	20.88	+0.8
20.25	22.1	20.88	+0.03	16.6	21.08	+1.3	17.2	21.05	−0.2	11.8	21.41	+1.1	15.9	21.11	+1.9
20.75	—	—	—	24.6	21.32	+2.5	20.3	21.43	+1.6	16.8	21.57	+1.8	—	—	—
Mean		20.87	±0.7		20.80	±0.9		21.09	±0.8		21.18	±1.6		20.71	±1.1

the true equivalence point by less than 0.5%. It may be further observed that if a sufficiently large number of measurements of ΔE is made, suitable criteria of rejection may be applied in order to eliminate the effect of gross errors in measurement on the result.[1]

Influence of Assumptions on Theoretical Treatment.

Equations (8) and (12) express the theoretical curve for the differential titration of a weak acid by a strong base, within the limits set by the validity of the assumptions made in the derivation of the equations. The chief assumptions are: (1) constancy of total volume of the solution: (2) validity of the Mass Action Law; (3) complete dissociation of the salt; (4) non-dissociation of the weak acid; (5) that hydrolysis is negligible.

(1) The total volume may be kept practically constant by making the ratio between volume of reagent required and original volume of solution very small; when this is not done suitable correction may be applied to equations (8) and (12). Another source of error is the temporary removal from the sphere of reaction of a small portion of the solution by isolating it in the capillary of the differential electrode. This has the effect of making [S] variable, whereas in the foregoing derivations it was assumed constant. ΔF is not $\frac{\Delta[B^+]}{[S]}$, as assumed, but

$$\frac{\Delta[B^+]}{[S] - R\,[S]\,(1 - F)}.$$

where R is the ratio of the isolated volume to the total volume. The correction, from the ratio between apparent ΔF and true ΔF, is, therefore, $R(1-F)\Delta F$. This correction term is at all times small and approaches zero as R is made smaller or as F increases. The actual correction for our experiments where $R = 0.02$ is negligible except in the region where $F = 0.5$. The effect, in general, is to flatten the curve and slightly to broaden the end-point. On the alkaline side the correction term is similar in form but of opposite sign.

(2) The Law of Mass Action is unquestionably valid for weak electrolytes in dilute solution.

(3) Within the concentration range in which we are interested complete dissociation of the salt may be assumed without error.

(4) This assumption is justifiable except during the first portion of the titration. Thus, although 0.001 N HAc is more than 10% ionized when no salt is present, when the acid is half neutralized the error introduced in equation (8) is only 0.05% and diminishes towards zero as the equivalence point is approached.

(5) The error in equation (12) caused by the hydrolysis of the salt can be shown to be negligible. The hydrolysis constant is given by[2]

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[1] It is to be noted that the computed values of [S] in Table VI do not vary in a random manner from the means. For each titration there is exhibited a decrease of [S] to a minimum, followed by an increase. Determination of the physical cause of this trend would permit the application of correction terms to equation (13) and greatly increase the precision.

[2] Cf. Kolthoff and Furman: "Potentiometric Titrations," 23-29 (1926).

$$\frac{\text{k}_\text{w}}{\text{K}_\text{a}} = \frac{[\text{HAc}]\,[\bar{\text{O}}\text{H}]}{\bar{\text{A}}\text{c}} \tag{16}$$

In equation (18) [HAc] may be set equal to $\text{k}_\text{w}/\text{x}$, where x is the concentration of hydrion resulting from the hydrolysis reaction, since by this reaction HAc and $\bar{\text{O}}\text{H}$ are formed molecule for molecule; whereas $[\bar{\text{O}}\text{H}]$ is proportional to the total hydroxyl concentration contributed by hydrolysis and by the added strong base. Making these substitutions,

$$\frac{\text{k}_\text{w}}{\text{K}_\text{a}} = \frac{1}{[\text{S}]}\left(\frac{\text{k}_\text{w}}{\text{x}}\right)\left\{\frac{\text{k}_\text{w}}{\text{x}} + [\text{S}]\,(\text{F} - 1)\right\},$$

and

$$\text{x} = \frac{1}{2}\,\text{K}_\text{a}\,(\text{F} - 1) - \frac{1}{2}\sqrt{\text{K}_\text{a}^2\,(\text{F} - 1)^2 + 4\,\frac{\text{k}_\text{w}\text{K}_\text{a}}{[\text{S}]}}\;. \tag{17}$$

The hydrolysis error is greatest near the neutral point (i.e., as F ⟶ 1). To gain a conception of the magnitude of the error consider the titration of 0.001 N HAc. Let F = 1.05 and ΔF = 0.025. Calculation from equations (12) and (19) shows that the error does not affect the true ΔE of 12.6 millivolts within the first three significant figures.

The Hypothetical Quinhydone Endpoint.

MacInnes,[1] in making acidimetry titrations by the differential method, found that in the presence of quinhydrone a second maximum was obtained in the curve shortly after the first maximum which indicated the main endpoint. MacInnes attributed this second endpoint to the dissociation of quinhydrone as a weak acid. Rabinowitsch and Kargin,[2] repeating this work (not however by direct measurement of the differential curve) conclude that the second maximum is caused by carbon dioxide and not by quinhydrone. These authors claim that when the titrations were carried out in the presence of an inert gas the second maximum did not appear. While our results are not, perhaps, to be regarded as strictly comparable with those of the other workers owing to the great difference between the concentration ranges in which we worked, we are able to state that we have had no indication of the existence of this second endpoint. The marked irregularities which we observed just on the alkaline side of the equivalence point we believe to be due to complicated changes of unknown character in the quinhydrone. We worked at all times in an atmosphere of inert gas, since the presence of air made it impossible even to obtain the first endpoint.

Summary

1. An apparatus and method for the differential potentiometric titration of weak acids in concentrations as low as 0.0004 N have been described.

2. The theory of the differential method is presented, and methods for estimating the endpoint are deduced therefrom.

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[1] MacInnes: Z. physik. Chem., Cohen-Festband, 217 (1927); J. Am. Chem. Soc., **48**, 2831 (1926).

[2] Rabinowitsch and Kargin: Z. Elektrochemie angew. physik. Chem., **34**, 311 (1928).

New York, N. Y.

ON THE PHYSICS OF THE ICE CREAM MIX

I A Relationship Between Basic Viscosity and the Whipping Capacity of Ice Cream Mixes

BY ALAN LEIGHTON AND OWEN E. WILLIAMS*

8 9A 99

The purpose of this paper is to report the results of a simple series of experiments which demonstrates that under certain restricted conditions the whipping capacity of an ice-cream mix is inversely related to the basic viscosity of the mix.

Two papers dealing with the basic viscosity of ice-cream mixes have already been published by these authors. The first paper[1] showed that the beaters in the ice-cream freezer destroy the structural viscosity of the ripened ice-cream mix, and that simple relationships between concentration and this stirred-out or basic viscosity can be demonstrated The second paper[2] showed the relationship between temperature and basic viscosity values It was emphasized in these papers that if any relationship existed between the viscosity of the mix and the whipping capacity, this relationship would be found between the basic viscosity value and the whipping capacity rather than between structural viscosity and whipping capacity.

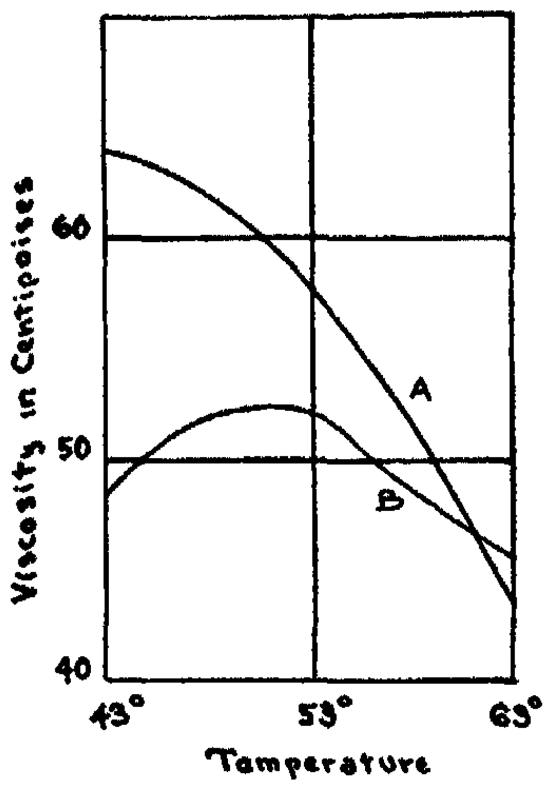

FIG. 1
Variation of Basic Viscosity with Temperature of Homogenization. Pressure 3000 lbs. per sq. in.

Later work has shown that under somewhat limited conditions a relationship between basic viscosity and whipping capacity does exist. To show such a relationship, the problem is to vary only those factors in the complicated ice-cream mix that determine the basic viscosity value, without at the same time varying appreciably other factors which also affect the whipping capacity of the mix It appears that this can be accomplished by the simple expedient of homogenizing portions of a mix at different temperatures without varying the pressure Under these circumstances a number of experiments upon ice-cream mixes of normal average composition have shown that at least two different conditions may exist

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* Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.

[1] J. Phys. Chem., 31, 596 (1927).

[2] J. Phys. Chem., 31, 1663 (1927).

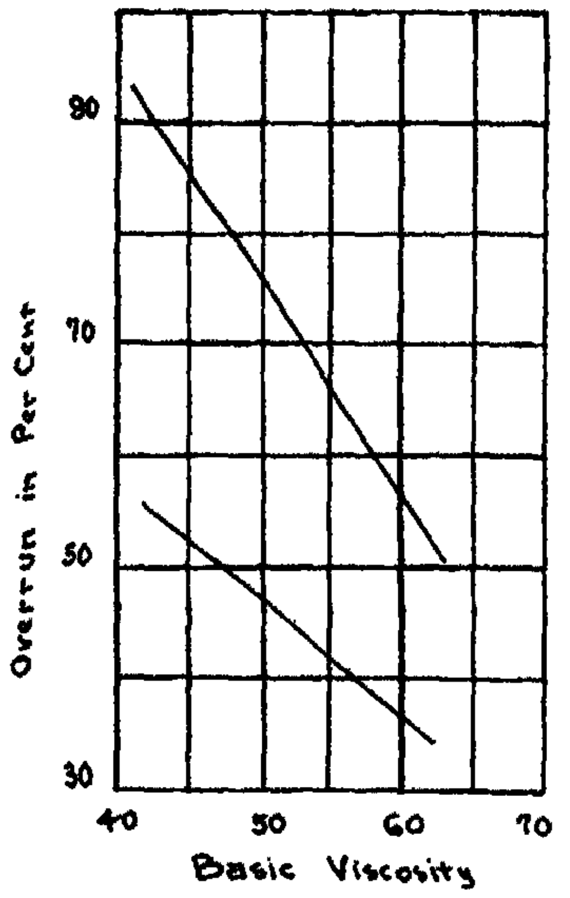

FIG. 2a
Relation of Viscosity to Overrun, Case A.

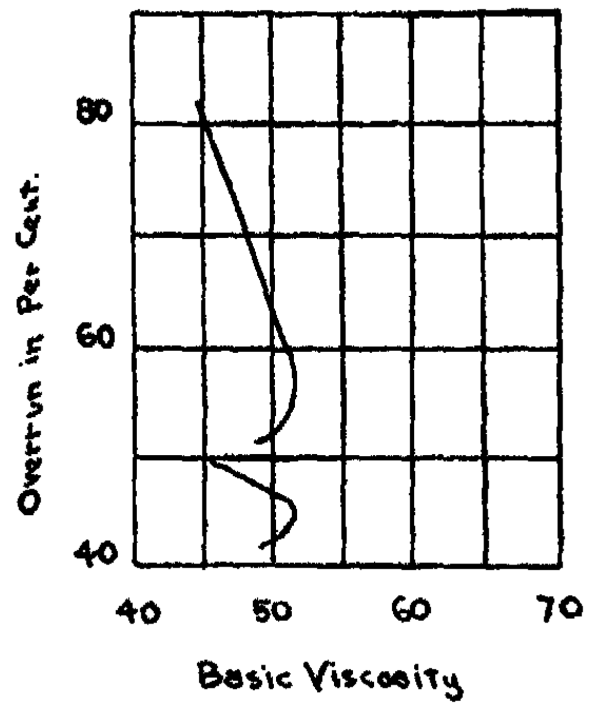

FIG. 2b
Relation of Viscosity to Overrun, Case B.

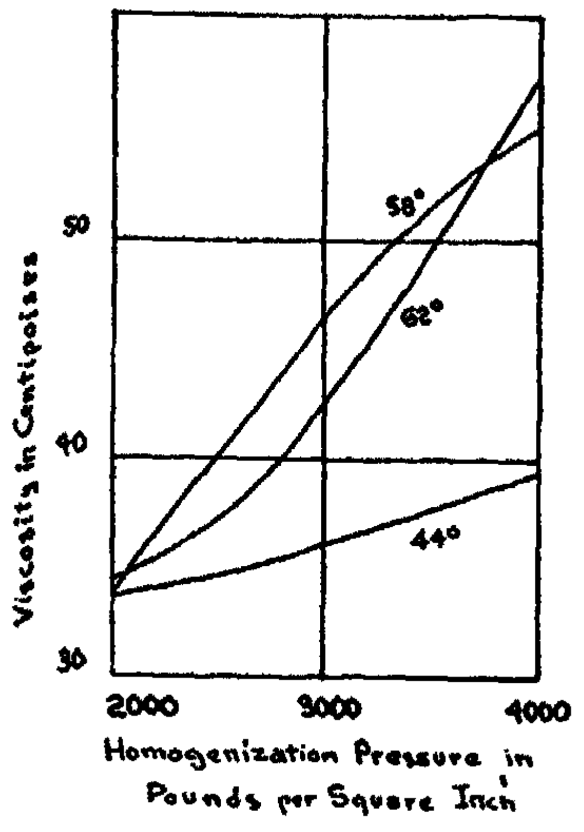

FIG. 3
Effect of Homogenization Pressure upon Basic Viscosity of Ice Cream Mixes.

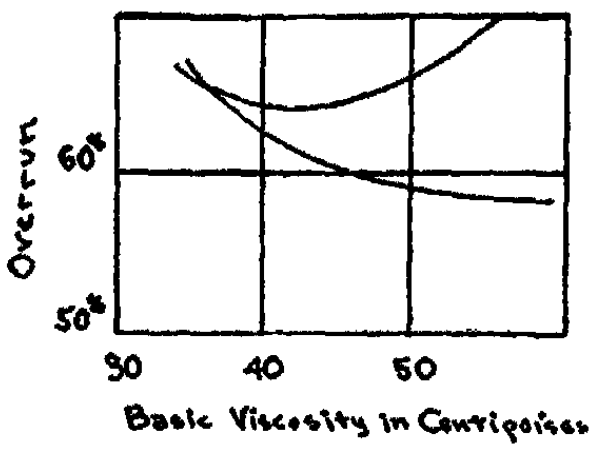

FIG. 4
Variation of Overrun with Viscosity when different Homogenization Pressures have been used to vary the Basic Viscosity.

Typical of these two possible conditions are the measurements of the two mixes designated in this paper as A and B. (See Table I and Fig. 1). In Mix A, a continuous decrease in basic viscosity with increase of the homogenization temperature is shown. In Mix B, the basic viscosity increases with increase in homogenization temperature to a maximum, then decreases. It is probable that in Mix A this same maximum exists but at a temperature lower than the minimum temperature recorded in these experiments.

The whipping capacity of the different portions of the two mixes was measured in two ways: First, portions of the mixes were frozen in the 6-gallon, horizontal, brine-cooled, power-driven ice-cream freezer. With the brine on continuously, the maximum overrun was reached in each case in 8 minutes. Second, other portions of the mixes were frozen in a battery of three, 2-quart, hand-type freezers which were also electrically driven and were surrounded by cold brine. Here the cans were opened and the overrun measured after 15 minutes of freezing. The complete data and curves are given in Table I and Figs. 2a and 2b.

TABLE I

The relation between homogenization temperature, basic viscosity, and overrun as obtained in large and small freezers. Mix A where no maximum exists in the homogenization-viscosity curve—Mix B where such a maximum exists

Homogenization 3000 pounds per square inch Temp. (°C)	Basic viscosity cp.	Overrun Large freezer per cent	Overrun Small freezer per cent
		Mix A	
43	64.2	51	—
48	61.1	54	35
53	58.2	60	38
58	51.1	73	—
63	43.5	88	54
		Mix B	
43	48.3	52	42
48	52.2	55	—
53	52.2	60	47
58	48.5	67	48
63	45.8	77	41

The curves and data show clearly that an inverse linear relationship between whipping capacity and basic viscosity exists over the whole experimental range in Mix A and over that range in Mix B where, with increased temperature of homogenization, the values of basic viscosity decrease.

Because of this simple relationship between whipping capacity and basic viscosity, the assumption is made that within the experimental range of these experiments where this relationship exists the variations in the temperature of homogenization have altered only those factors of which the basic viscosity determination is a measure. It is equally apparent that, since no simple relationship between basic viscosity and whipping capacity exists in the Mix B when the viscosity is increasing with homogenization temperature, basic viscosity is not the only factor to influence whipping capacity. This becomes more apparent when it is considered that no simple relationship between basic viscosity and whipping capacity exists when the viscosity of the ice-cream mix is varied by altering the pressure of homogenization while the temperature of homogenization remains constant. (See Table II, Fig. 3 and 4.)

TABLE II

Relation of homogenization pressure to basic viscosity and overrun at different temperatures

Homogenization pressure per square inch	Temp. 44°C		Temp. 58°C		Temp. 62°C	
	viscosity	overrun	viscosity	overrun	viscosity	overrun
pounds	cp.	per cent	cp.	percent	cp.	per cent
2000	34.1	—	34.2	68	34.0	35
3000	35.9	—	46.4	65	42.3	61
4000	39.5	—	55.0	70	57.5	58

A separate study is being made of these other factors which influence whipping capacity. The conclusion is drawn from the experiments described in this paper, however, that, other conditions being unchanged, a simple inverse relationship exists between basic viscosity and the whipping capacity of the normal ice-cream mix.

THE BASIC VISCOSITY AND PLASTICITY OF ICE-CREAM MIXES

ALAN LEIGHTON AND FLOYD ERVIN KURTZ[*]

39A-100

Two important papers dealing with the plasticity of milk and its products[1] have recently been published from the laboratories of the Dairy Department of Cornell University. Exact measurements showed that even skim milk was very slightly plastic. Interesting data were also given concerning the plasticity of the normal unstirred ice-cream mix.

Casual unpublished measurements made by one of the authors of this paper had shown previously that the stirred out or basic viscosity of an ice-cream mix could for all practical purposes be considered a true measurement. In view of the Cornell work it seemed desirable to check these measurements, particularly since it had been shown in these laboratories that simple relationships do exist between basic viscosity, concentration, temperature, and whipping capacity of the mix, and since it might develop that certain corrections would have to be made in the expression of these relationships. At the same time it seemed desirable to obtain in a general way data showing which constituents of the mix most markedly affect the plastic properties, i.e., yield-value and consistency of the mix. It is not safe to assume that a stirred ice-cream mix is plastic even if skim milk exhibits these properties, since the presence of sugar and gelatin in the liquid phase of the mix markedly alters the physical properties of the system as a whole.

The basic viscosity and plasticity measurements were made in the same general way as described in previous papers; i.e., the liquid under measurement was drawn by suction against gravity through the capillary tubes of the viscometers. This method was used so that in the case of the basic-viscosity measurements no time would be lost in filling the viscometer and bringing it to the proper temperature.

The complete procedure of a measurement follows: First the air pressure within a 5-gallon reservoir was reduced to the proper value for the experiment. This tank was connected to the house vacuum line, a mercury pressure regulator being inserted between the vacuum cock and the tank, which permitted air to bubble into the system through a predetermined depth of mercury. The reduced pressure as read on a mercury manometer was maintained very accurately in this way, provided the cock in the vacuum line was closed to the point which permitted but a small stream of air to pass steadily through the mercury of the regulator. The pressure tank was connected to the viscometer by means of pressure tubing and a glass stop-cock.

If the basic viscosity of a mix were to be measured, the mix was poured into a specially constructed 2-quart freezer and stirred vigorously for one-

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[*] Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.

[1] J. Agr. Research, 36, 647; J. Dairy Sci., 11, 380 (1928).

half hour while the freezer was immersed in an accurately regulated thermostat at zero degrees centigrade. Care was taken to fill the freezer completely so that no air would be incorporated into the mix. If the unstirred viscosity, or plasticity, were to be measured a 2-quart can of the mix which had been standing since preparation at approximately zero degrees centigrade was placed in a special rack within the thermostat and allowed to stand for one-half hour to reach the temperature of the bath.

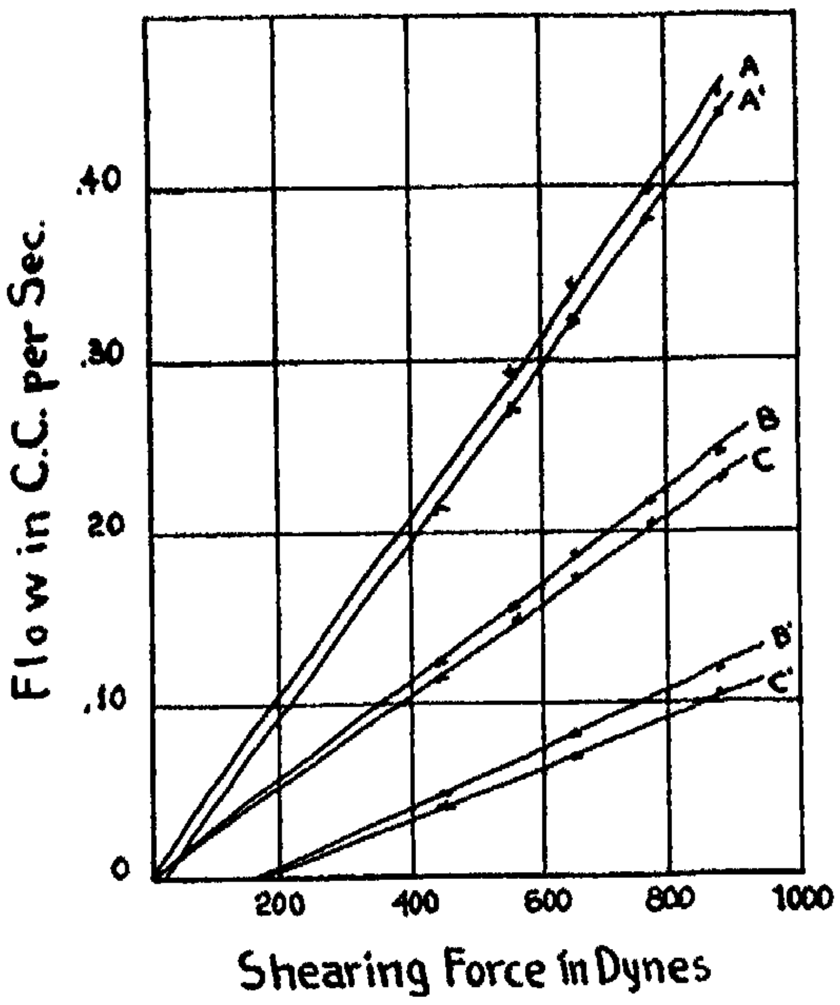

FIG. 1

A—No gelatin
B—63° Homogenization
C—43° Homogenization

To make the actual determination, the viscometers, made by sealing capillary tubing onto pipette bulbs, were immersed in the mix to a definite depth and connected to the low pressure reservoir. The interval of time required to fill them was noted with the aid of a 1/10 second stop watch.

In the course of this work two viscometers of the dimensions given in Table I were used.

TABLE I

Dimensions of viscometers A and B

	Volume	Capillary radius	Capillary length
	cc	centimeters	centimeters
Viscometer A	8.223	0.05044	8.492
Viscometer B	24.440	0.04957	8.808

The degree of vacuum in the reservoir was measured on a mercury gauge. Five different pressures were used in this work. In determining the shearing force at the walls of the capillary tubing, the pressure correction for the height of the liquid column in the viscometer was evaluated for each viscometer by standardizing the instrument with a viscous cane-sugar solution of known density at all five pressures, plotting the straight line flow against reservoir pressure, and extrapolating this line to the pressure axis. The pressure above zero at the line intersection gives the proper correction for a liquid of the same density as the cane-sugar solution used in the standardization, and gives data from which the average hydrostatic pressure of any liquid in the viscometer may be calculated.

The capillary dimensions of the viscometers were purposely chosen of fairly large radius in order that the time of flow of liquid be not overlong, since in the stirred out viscosity determinations it seemed desirable to make the measurement before there could be an appreciable recovery in the viscosity of the mix. There would also be less danger of trouble from clogging. The accuracy under these conditions is all that could reasonably be desired. For absolutely accurate results, however, smaller capillaries should probably be used, and, as Sharp[1] has pointed out, the possible effect of capillary size needs further study.

Experimental

The first experiments were conducted to ascertain whether there was an appreciable yield-value in ice-cream mixes which had been stirred. Out of twenty-five to thirty mixes only two demonstrated a measurable yield-value, and these had been standing for about one week and were on the verge of spoiling.

In Table II and Fig 1 are given data of a number of typical experiments. The basic viscosity measurements are given for a mix without gelatin and for mixes containing a good grade of gelatin homogenized at different temperatures. The plasticity data for corresponding unstirred portions of the experimental mixes are also given.

As has already been pointed out, the measurements upon the mixes which had been stirred exhibited no plastic properties detectable within the limits of experimental error. The conclusion is reached, therefore, that the basic viscosity measurement may still be considered as the true measurement of a physical property. Unstirred ice-cream mixes, even without the presence of gelatin, do, however, show a slight degree of friction when run through the capillary tubes of the viscometers.

The most striking effects, however, are produced by the presence of gelatin. It is seen at once that the gelatin not only imparts an appreciable yield-value to the mix, which value is in all probability a measure of the

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[1] Private communication.

TABLE II

Basic viscosity-plasticity data on three stirred and unstirred typical mixes

	Force	Basic viscosity		Plasticity of structure		Yield value
		Delivery	Viscosity	Delivery	consistency	
	dynes	cc.	cp.	cc.		dynes
	1. 446.7	—		0.2167		
Mix 1	2. 562.8	0.2932		0.2724		
No gelatin	3. 653.4	0.3470	19.43	0.3213	19.71	20
	4. 775.8	0.4001		0.3807		
	5. 886.3	0.4556		0.4422		
	1. 446.7	0.1155		0.04033		
Mix 2	2. 562.8	0.1455		—		
Gelatin	3. 653.4	0.1714	38.62	0.06987	69.72	175
homogenized	4. 775.8	0.2041		—		
at 43°C.	5. 886.3	0.2311		0.10270		
	1. 446.7	0.1269		0.04809		
Mix 3	2. 562.8	0.1579		—		
Gelatin	3. 653.4	0.1900	36.07	0.08299	59.20	170
homogenized	4. 775.8	0.2194				
at 63°C.	5. 886.3	0.2474		0.12100		

structural strength of the gel, but the consistency of both the stirred and unstirred mix with gelatin is markedly greater than would be the case if gelatin were not present.

The conclusion is reached, therefore:

That the basic viscosity value of an ice-cream mix should be considered a true measurement. This conclusion is made in spite of the fact that the viscosity of the mix is markedly affected by gelatin which gives both a yield-value and greater consistency to the unstirred mix.

VISCOSITY-PLASTICITY MEASUREMENTS OF THE EFFECT OF GELATIN ON ICE-CREAM MIXES

BY FLOYD ERVIN KURTZ* 39A101

Numerous methods of testing gelatin are known. Dahlberg, Carpenter and Hening[1] have reviewed and criticized, in the light of their own researches, some of the more important. It is the purpose of this paper to consider the significance of basic viscosity-plasticity measurements in grading gelatin for the manufacture of ice cream.

Experimental

For the purpose of this report equal concentrations of six commercial gelatins were used in making ice-cream mixes of the following formula:

Milk-solids-not-fat	10%
Fat	12%
Sucrose	14%
Gelatin	0.25%
Water	63.75%

Another mix was made identical, except that no gelatin was added. After the mixes had stood for 24 hours at the same temperature (approximately 0°C.) measurements were made to determine the basic viscosity of each. Leighton and Kurtz[2] discuss the appropriateness of the term " basic viscosity" as applied to the values obtained from these measurements. They also describe the method of making these measurements, which consists, briefly, in beating out the structure of the ice-cream mix at 0°C. until a constant value is obtained when the sample is drawn through a calibrated pipette by a constant vacuum pressure. The dimensions of this 8.2 cc. pipette have been recorded. Table I expresses in centipoises the values obtained for the basic viscosity of the seven mixes. Fig. 1 shows graphically the relationship between the viscosities of these mixes.

After standing 48 hours at 0°C. other samples of the same mixes were measured for plasticity. The method used in making these measurements was the same, with one exception, as that used in measuring the basic viscosity — the exception being that, instead of beating out the structure, precautions were taken that it should be broken only by the passage of the material through the plastometer. Table II and Fig. 2 show the results of these measurements. The consistencies are tabulated in centipoises and the yield values in dynes.

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* Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture.

[1] Dahlberg, Carpenter and Hening: Ind. Eng. Chem., 20, 516 (1928).

[2] J. Phys. Chem., 33, 1485, (1929).

TABLE I

Variation of basic viscosity of ice cream mixes with different grades of gelatin

Gelatin sample No.	Shearing force dynes	Volume delivered cc. per sec.	Basic viscosity centipoises
No gelatin	1. 446.7	1. —	19.43
	2. 562.8	2. .2932	
	3. 653.4	3. .3470	
	4. 775.8	4. .4001	
	5. 886.3	5. .4556	
1	1. 446.7	1. —	29.41
	2. 562.8	2. .1895	
	3. 653.4	3. .2253	
	4. 775.8	4. .2637	
	5. 886.3	5. .3035	
2	1. 446.7	1. —	29.34
	2. 562.8	2. .1929	
	3. 653.4	3. .2299	
	4. 775.8	4. .2662	
	5. 886.3	5. .3063	
3	1. 446.7	1. —	37.52
	2. 562.8	2. —	
	3. 653.4	3. —	
	4. 775.8	4. .2082	
	5. 886.3	5. —	
4	1. 446.7	1. —	24.65
	2. 562.8	2. —	
	3. 653.4	3. —	
	4. 775.8	4. .3169	
	5. 886.3	5. —	
5	1. 446.7	1. —	21.93
	2. 562.8	2. —	
	3. 653.4	3. —	
	4. 775.8	4. .3530	
	5. 886.3	5. .4070	
6	1. 446.7	1. —	28.01
	2. 562.8	2. .2016	
	3. 653.4	3. —	
	4. 775.8	4. —	
	5. 886.3	5. .3185	

TABLE II

Variation of the consistency and yield value of ice cream mixes with different grades of gelatin

Gelatin sample No.	Shearing force dynes	Volume delivered cc. per sec.	Consistency centipoises	Yield value dynes
No gelatin	1. 446.7	1. .2167	19.71	20
	2. 562.8	2. .2724		
	3. 653.4	3. .3213		
	4. 775.8	4. .3807		
	5. 886.3	5. .4422		
1	1. 446.7	1. —	39.63	35
	2. 562.8	2. .1338		
	3. 653.4	3. —		
	4. 775.8	4. .1865		
	5. 886.3	5. .2164		
2	1. 446.7	1. —	39.67	125
	2. 562.8	2. .1121		
	3. 653.4	3. .1344		
	4. 775.8	4. .1615		
	5. 886.3	5. .1933		
3	1. 446.7	1. —	55.03	170
	2. 562.8	2. .07168		
	3. 653.4	3. —		
	4. 775.8	4. .1079		
	5. 886.3	5. .1311		
4	1. 446.7	1. —	25.23	75
	2. 562.8	2. .1954		
	3. 653.4	3. —		
	4. 775.8	4. .2769		
	5. 886.3	5. .3238		
5	1. 446.7	1. —	25.03	20
	2. 562.8	2. .2202		
	3. 653.4	3. —		
	4. 775.8	4. .3029		
	5. 886.3	5. .3485		
6	1. 446.7	1. —	30.37	115
	2. 562.8	2. —		
	3. 653.4	3. —		
	4. 775.8	4. .2187		
	5. 886.3	5. .2558		

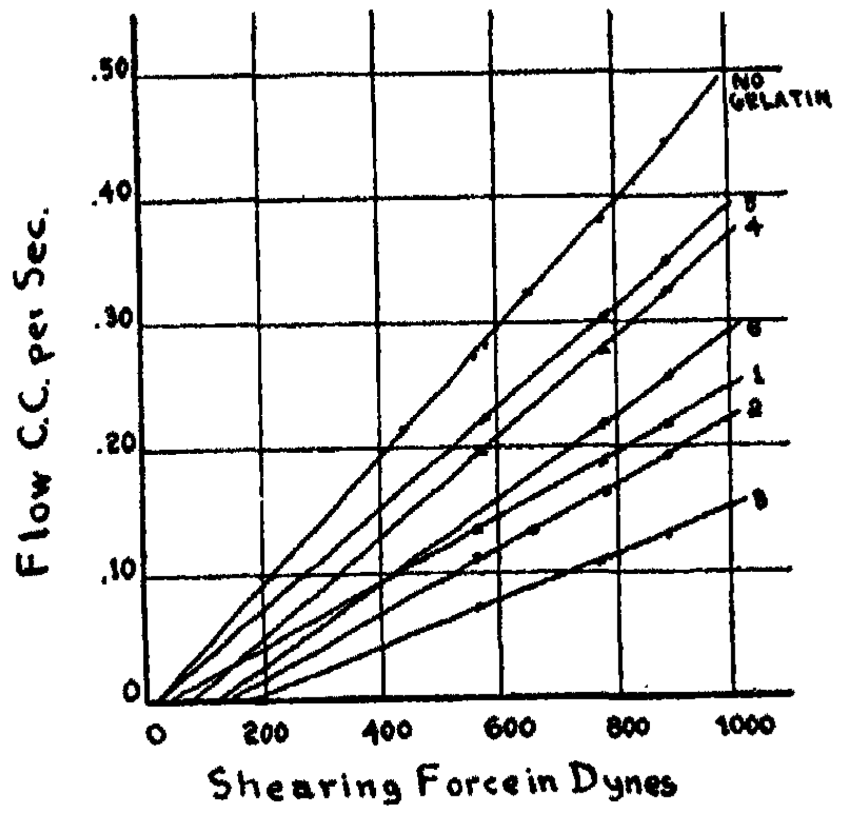
Flow C.C. per Sec.
.50
.40
.30
.20
.10
0
0
200
400
600
800
1000
Shearing Force in Dynes
NO GELATIN
5
4
6
1
2
3

FIG. 1

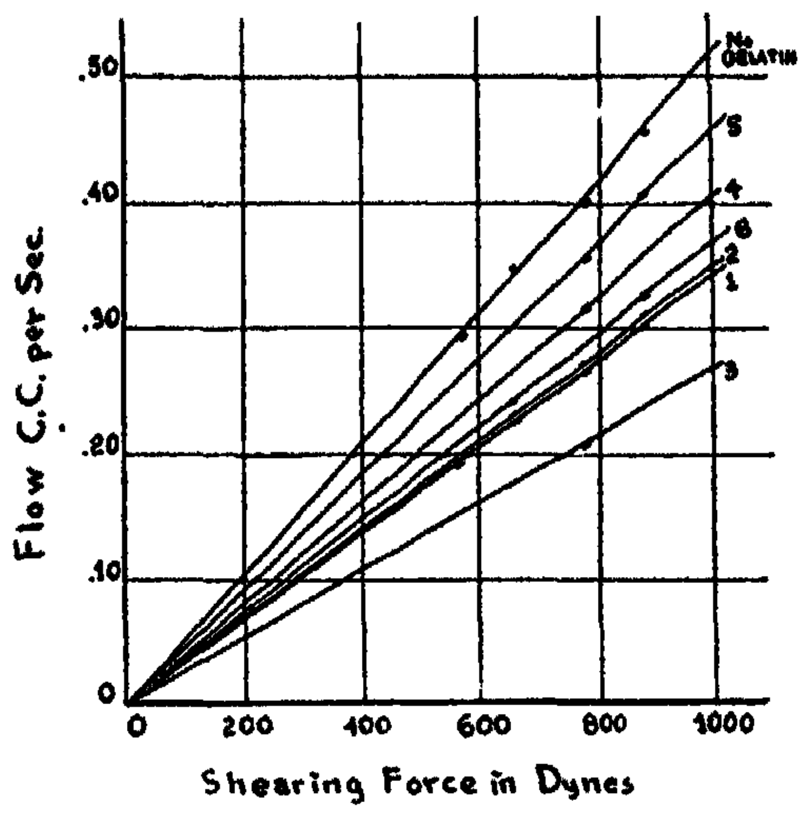
Flow C.C. per Sec.
.50
.40
.30
.20
.10
0
0
200
400
600
800
1000
Shearing Force in Dynes
No GELATIN
5
4
6
2
1
3

FIG. 2

Discussion

Previous tests, for the most part, have failed to discriminate between the effects produced by different gelatin samples on the various fundamental physical properties of the ice-cream mix. The method employed, as a rule, has measured either the effects on one to the exclusion of those on the other physical properties of the mix, or the resultant value of the combined effects on several of the basic characteristics of the mix. In so far as the various fundamental physical properties of a mix may differently affect the manufactured product, it would be desirable in the test to be applied to the mix to differentiate these properties.

In this investigation measurements have been made to determine the effects produced by equal concentrations of different gelatins, in otherwise identical ice-cream mixes, on the basic viscosity, consistency, and yield value. More research will be necessary to correlate these basic values of the mix with the quality of the frozen ice cream. As this correlation is achieved, such measurements as have been made in this study will be of value in obtaining the desired qualities in the manufacture of ice cream for, as references to Figs. 1 and 2 will show, a considerable variation can be obtained not only in the quantitative measure of any one, but also in the relation to each other of the three properties here measured.

Basic viscosity quite likely affects the growth of ice crystals in the freezer. Since the beaters furnish many nuclei for crystallization, an increased basic viscosity of the mix would serve to hinder the growth of these crystals. Dahlberg, Carpenter and Hening's* data on gelatins indicate that there is no relation between basic viscosity of mix and overrun. From a slightly different standpoint, however, Leighton and Williams[1] found that overrun per unit time is considerably affected by the basic viscosity and seems to bear an inverse relation to it.

In the gelatin mixes, which are known to have a gel structure, the yield value should be interpretable as the force necessary to break this structure. On this hypothesis, then, the yield-value is a measure in an absolute unit, the dyne, of the structural strength produced in the mix by the gelatin. In reality, a correction is necessary. This is due to the slight structure of the ice-cream mix not dependent upon the presence of the gelatin. Reference to Fig. 2 will show that the non-gelatin mix has a yield-value of 20 dynes; so, if this were subtracted from each of the values obtained for the gelatin mixes, there would be obtained an absolute measure of the structural strength due to the presence of the gelatin. After sufficient force is applied to a mix to break down its structure and establish flow through the capillary, the volume delivered per unit time as a function of the total force applied minus the yield-value gives a linear graph of the consistency, which can be considered analogous to the viscosity of a truly viscous substance.

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* Loc. cit.

[1] J. Phys. Chem., 33, 1481 (1929).

The effect of the consistency of the mix on the frozen ice cream is not known and indeed is difficult even to conjecture. It is possible that gumminess may depend upon the consistency of the mix, although this is, by no means, certainly known. Further researches quite possibly will reveal relations unseen at present.

Concerning the relation between yield-value and the properties of the frozen ice cream: It is rather generally accepted that the structure of an ice-cream mix during the hardening period obstructs the growth of ice crystals and, in this way, influences the smoothness of the product. Likewise, structure should have an inhibitory influence on the crystallization of lactose or sucrose. By preventing collapse of the frozen product, structure prevents loss from dipping and also preserves the dispersion of the air phase, thus preventing the development of sogginess.

Conclusion

It is theoretically plausible that basic viscosity, consistency, and yield-value of the mix have individually peculiar relationships to the properties of the frozen ice cream. A correlation of the values of these physical measurements with the nature of the manufactured ice cream will depend, for the most part, on future research. As this correlation is developed, the value of the combined basic viscosity-plasticity measurements for grading gelatin used in ice cream manufacture will be twofold: 1. Values are obtained in fundamental physical units; 2. In as far as these basic physical properties of the mix affect differently the properties of the frozen ice cream, their individual measurement would better enable the operator to control the properties of the manufactured product.

Summary

1. To determine basic viscosity, yield-value, and consistency, measurements have been made on seven ice-cream mixes, six of which, otherwise identical, contained equal concentrations of different commercial gelatins, and one of which contained no gelatin. The results are tabulated.

2. The value of these measurements in grading gelatins for ice cream manufacture is discussed.

THE ELECTRICAL CONDUCTIVITY OF ORGANIC ACIDS IN WATER, ALCOHOLS, AND ACETONE, AND THE ELECTRONIC STRUCTURES OF THE ACIDS*

BY HERSCHEL HUNT WITH H. T. BRISCOE

In a previous paper[1] the authors presented data dealing with the conductances of twenty-four organic acids in water and ethyl alcohol. The work reported in this paper represents an extension of that study to solutions of some of these acids in methyl, propyl, and butyl alcohol, and acetone. There is a pronounced lack of data dealing with the effect of properties and constitution of such solvents upon the ionization and conductance of solutions of weak electrolytes.

This paper also includes the work done to date upon the study of ethyl alcohol solutions of certain dibasic acids, a few acids whose molecules contain double bonds, and several aromatic acids not included in the previous report. The dissociation constants of various benzoic acid derivatives have been calculated from the values of the limiting conductivities of HCl, NaCl, and the sodium salts of the acids at 30°C.

Experimental

The alcohols were treated with 20 cc. of sulphuric acid and 20 cc. of water per liter to free them from amines and were then distilled. They were freed from aldehydes by distilling from an alkaline silver nitrate solution. High-calcium hydrated lime was dehydrated in an electric furnace at 600-700°C. Each alcohol was dehydrated by refluxing one liter of alcohol with 500 gms. of this lime for eight hours. After distillation, the product was again refluxed with 200 gms. of lime, and the alcohol was distilled. After fractional distillation the methyl alcohol was found to have a specific conductance of $3.5\text{-}2.69 \times 10^{-7}$ reciprocal ohms. This conductance was lowered to 2.45×10^{-7} reciprocal ohms by distilling the alcohol from metallic calcium. Conductance measurements were made at 30°C.

Ethyl alcohol prepared in the above manner had a specific conductance of 75×10^{-9} reciprocal ohms; normal propyl alcohol gave a specific conductance of 9.17×10^{-9} reciprocal ohms; and normal butyl alcohol gave a specific conductance of 9.12×10^{-9} reciprocal ohms. The specific gravity of the ethyl alcohol at 25°C. varied from 0.78508-0.78510. Pure alcohol[2] has a specific gravity of 0.78507 at this temperature. The water content of our alcohol is therefore less than 0.005 N.

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* This paper is a part of a thesis submitted by the first-named author as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Indiana University.

[1] Hunt and Briscoe: J. Phys. Chem., 33, 190 (1929).

[2] "International Critical Tables," 3, 117.

Acetone was prepared by long standing over calcium chloride. It was then fractionally distilled with a thermometer and later with a long fractionating column. The last distillation was performed with the use of a block tin condenser. Acetone, thus purified, had a specific conductance of 12.8×10^{-8} reciprocal ohms at 30°C.

The bridge assembly was the same as that used in the previous work, except for the alterations described below. The microphone hummer was replaced by a Type E Vreeland Oscillator. This instrument, as well known, produces a pure sine wave of constant frequency independent of fluctuations in the actuating direct current. It is also noiseless in operation and may be conveniently started and stopped. Although the frequency may be altered, all measurements made in this work were made with the oscillator set to give a wave of 1000 cycles per second.

Variable air condensers (5×10^{-4} to 12×10^{-7} microfarads) were placed in series with the resistance arm of the bridge to overcome electrode effects and to aid in producing a definite and easily determined minimum in the telephones.

Curtis coils (10–110,000 ohms) were used for resistances above 1000 ohms in order to aid in the elimination of errors due to inductance and capacity. These coils had an accuracy of 0.04% and were checked against a standard resistance. Resistances below 1000 ohms were measured by means of a small Leeds and Northrup calibrated, four-dial box.

The cells used in the previous work were employed for the solutions of greatest conductivity. For solvents and very feebly conducting solutions, a cell similar to that described by Danner and Hildebrand[1] was used. This cell had a constant of 0.00366685. All cell constants were frequently checked.

The bath, bridge, and method of cleaning apparatus, calibration, filling the cells, and preparing solutions have been described in the previous paper.

Data

In the following tables the molecular conductances of the acids are given for the various solvents. The temperature was 30°C. in each case. Blanks in the tables are due to the fact that some of the most dilute solutions were such feeble conductors that a significant reading could not be made or because of the insolubility of the acid in the solvent at these particular dilutions.

TABLE I

Monochloroacetic Acid

Dilution	MeOH	EtOH	PrOH	BuOH	Acetone
2	0.1451	0.0592	0.00288	0.00157	0.0091
8	0.5358	0.1111	0.00520	0.00267	0.0152
32	2.0314	0.2205	0.01122	0.00530	0.0369
128	8.0125	0.4809	0.03535	0.01251	0.0776
512	35.6723	1.1951	0.10357		0.2206
1024	62.9393	1.6363			0.2509

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[1] Danner and Hildebrand: J. Am. Chem. Soc., **44**, 2824 (1922).

TABLE II
Dichloroacetic Acid

Dilution	MeOH	EtOH	PrOH	BuOH	Acetone
2	0.3375	0.2531	0.0182	0.0096	0.0232
8	0.6697	0.4576	0.0258	0.0131	0.0388
32	1.4030	0.8958	0.0455	0.0218	0.0777
128	3.3549	1.7619	0.0963	0.0523	0.1642
512	9.9886	4.3369	0.2037	0.1389	0.4567
1024	18.2681	7.6226	0.3118	0.2474	0.6854

TABLE III

Dilution	MeOH	EtOH	PrOH	BuOH	Acetone
2	1.7340	2.0474	0.0649	0.0249	0.0372
8	3.3155	3.6805	0.1051	0.0383	0.0575
32	6.8765	6.5904	0.1865	0.0673	0.0982
128	14.0599	11.7716	0.3562	0.1290	0.2797
512	30.4619	20.6543	0.6984	0.2639	0.7110
1024	40.7705	27.3858	0.9627	0.3207	0.8368

TABLE IV
Cyanacetic Acid

Dilution	MeOH	EtOH	PrOH	BuOH	Acetone
2	0.3790	0.2073	0.0549	0.0295	0.3356
8	0.5915	0.3292	0.0676	0.0365	0.3808
32	1.0778	0.5805	0.0807	0.0479	0.4460
128	2.3813	1.0989	0.1072	0.0639	0.5347
512	7.6400	2.1651	0.1855	0.1129	0.6333
1024	15.0968	3.0183	0.2500	0.1323	0.6863

TABLE V
Glycollic Acid

Dilution	MeOH	EtOH	PrOH	BuOH	Acetone
2	0.0766	0.0416	0.0062	0.0035	0.0349
8	0.2094	0.0716	0.0077	0.0043	0.0457
32	0.6431	0.1210	0.0116	0.0068	0.0543
128	2.5744	0.2523	0.0225	0.0133	0.0856
512	10.7402	0.6065			0.1473
1024	20.1687	0.9072			0.1882

Table VI
Monochloroacetic Acid in Mixtures of Alcohols
(50% each by volume)

Dilution	MeOH-PrOH	MeOH-BuOH	EtOH-PrOH	EtOH-BuOH
2	0.0364	0.0336	0.0224	0.1092
8	0.1171	0.1097	0.0409	0.0369
32	0.4077	0.4040	0.0832	0.0812
128	1.5896	1.5819	0.1726	0.2240
512	6.4601	6.1683	0.3965	0.7162
1024	12.1364	11.9962	0.6176	1.3861

Table VII
Molecular Conductivity of Acids in Acetone

Dilution	Acetic Acid	Bromoacetic Acid	Iodoacetic Acid
2	0.0020	0.0059	0.0804
8	0.0039	0.0108	0.1346
32	0.0084	0.0340	0.1848
128	0.0247	0.0926	0.3538
512	0.0581	0.2525	0.6886
1024		0.4721	1.1392

Discussion of Results

The order of conductivity values for the various solvents is water, methyl, ethyl, propyl, and butyl alcohol for each acid studied. The solution of an acid in acetone has a conductance between that of ethyl and propyl alcohol, except in the case of trichloroacetic acid, in which case the values fall between those for propyl and butyl at most dilutions.

The dielectric constants[1] of the various solvents at 20°C. are:

Methyl alcohol	31.2	Butyl alcohol	19.2
Ethyl Alcohol	25.8	Acetone	20.7
Propyl alcohol	22.2		

The dielectric constant of acetone is nearer the value for butyl alcohol than that of any of the other alcohols, but the acetone solutions are better conductors than those of both butyl and propyl alcohol in most cases. This cannot be explained on the basis of fluidities. The fluidity of acetone is almost as much greater than that of methyl alcohol as the fluidity of the latter exceeds that of ethyl alcohol.[2]

It is at least interesting to note that the CH_3 group attached to the hydroxyl forms molecules of a solvent much weaker in ionizing power than water. Separation of the CH_3 group from OH by CH_2 (CH_3–CH_2–OH) does not greatly alter the ionizing power of the medium. The addition of a

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[1] Landolt-Börnstein: Tabellen, 2, 1036 (194 d).

[2] Ramsay and Shields: Z. physik. Chem., 12, 433 (1893).

second CH_2 group (CH_3-CH_2-CH_2-OH), however, again causes a very pronounced decrease in ionizing power. The third CH_2 group (CH_3-CH_2-CH_2-CH_2-OH) causes very little change. For instance, in the case of dichloroacetic, water solutions show conductances of 20–166 times the conductances in methyl alcohol, dependent upon the dilution. Ethyl alcohol solutions are 14–24 times better conductors than propyl alcohol solutions of the same acid concentration. The conductances in methyl alcohol solutions, however, are only 1.5–2.4 times those in ethyl alcohol and the values in propyl alcohol are only 1.3–2 times the conductances in butyl alcohol. These relations are shown graphically in Fig. 1. Regardless of the acid dissolved in the alcohols, the conductivities in the various alcohols stand in approximately the same proportion as mentioned here for dichloroacetic acid. The variations are probably very nearly within the range of experimental error. Most certainly the approximate variations are the same for different acids with the one exception of glycollic acid in the more dilute solutions in methyl and ethyl alcohol. The almost uniform variation in conductivity with change in solvent and the great variations between water and methyl alcohol, and between ethyl and propyl alcohol, with insignificant changes between methyl and ethyl, and propyl and butyl, have no direct relationship to the dielectric constants, fluidities, and association tendencies of the alcohols. It seems that they must be explained by the effect of the carbon-hydrogen group upon the power of the oxygen atom of the OH group to combine with the hydrogen ion of the acid. In other words, the presence of the methyl, ethyl, and other radicals affect the basicity or hydrogen accepting properties of the solvent.

As might be expected, the acceptance of hydrogen by the oxygen atoms of the hydroxyl groups will also be controlled somewhat by the nature of the substituent atoms or radicals in the acid molecule. The substitution of chlorine in the molecule of acetic acid causes the hydrogen atom of the carboxyl to be more easily detached through the influence of the negative chlorine upon the electron-sharing properties of the oxygen atoms of the carboxyl group. To the extent that it is freed, however, it may be expected that hydrogen ion will be accepted by the oxygen atoms of a particular alcohol to approximately the same extent and that the acceptance of H by the oxygen atoms of different alcohols will vary in a fairly constant ratio regardless of the acid which acts as solute. The absolute basicity or hydrogen accepting property of the solvent is determined by the electronegativity of the group that is attached to the hydroxyl radical of the alcohol.

It seems, therefore, that an equilibrium between the hydrogen attached to the oxygen atoms of the carboxyl group (and to various other atoms of its molecule which may act as donors[1] of free electron pairs) on the one hand, and the oxygen atom of the solvent molecules on the other, really determines the extent of ionization of the acid and the conductance of the solution. This equilibrium may be shifted in one direction or the other by substitutions in the molecule of solvent or acid.

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[1] Sidgwick, in his "Electron Theory of Valency," refers to an atom surrounded in whole or in part by unshared electron pairs as a "donor" atom.

The basicity or hydrogen-accepting property of acetone is believed to depend upon the presence of an enol modification. Such a modification has been assumed to account, at least in a measure, for its association and rather high dielectric constant. We note that acetone has a fairly constant ability to accept hydrogen ion, falling just below ethyl alcohol in this regard.

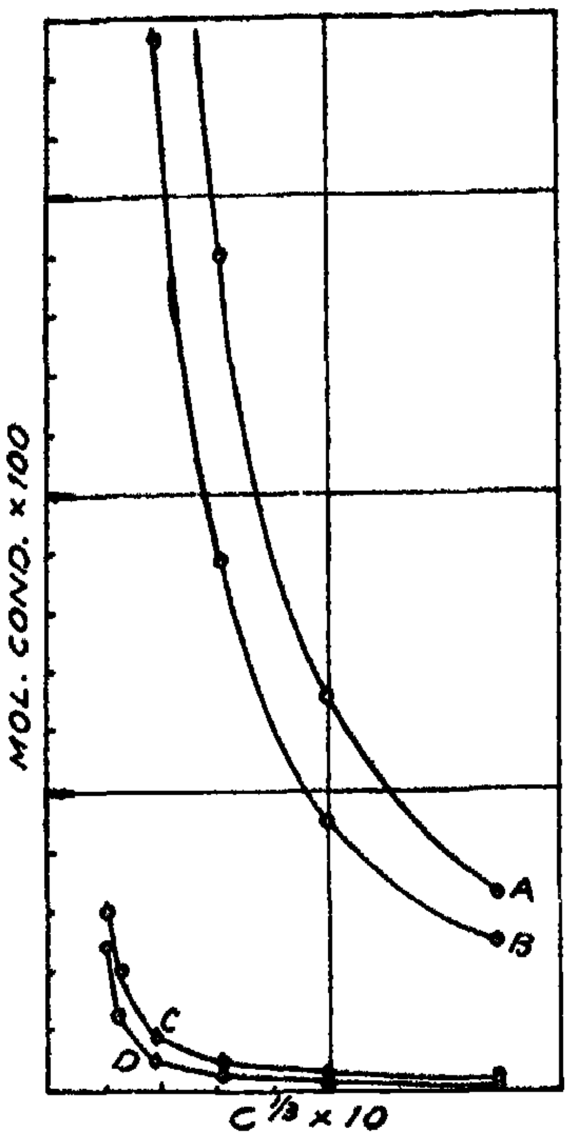

Fig. 1

A. MeOH Solutions
B. EtOH "
C. PrOH "
D. BuOH "

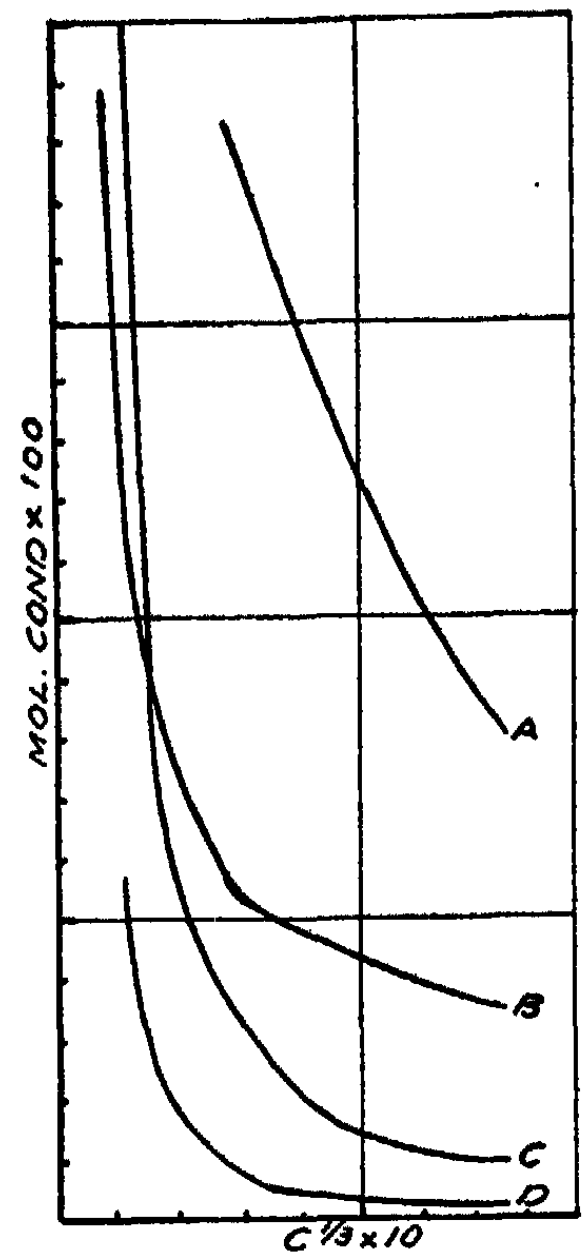

Fig. 2

A. Iodoacetic Acid
B. Glycollic Acid
C. Chloroacetic Acid
D. Acetic Acid

Its acceptance of hydrogen, as in the alcoholic solutions, is limited by the strength of the bonds by which hydrogen is attached to the donor atoms of its own molecule.

These facts and ideas lend support to the suggestions of Latimer and Rodebush[1] and others, that the dielectric constants, molecular association, and ionizing power of the solvent are not directly dependent upon one another, but are to be considered as individually dependent upon the molecular structure of the solvent and solute.

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[1] Latimer and Rodebush: J. Am. Chem. Soc., 42, 1419 (1920).

Brönsted[1] has defined the basicity constant of the solvent by means of the following equation:

$$K_A = K_{Acid} K_{Bas.}$$

in which K_A is the dissociation constant of the acid, K_{Acid} its acidity constant, and $K_{Bas.}$ is the basicity constant of the solvent. Assuming that the acids have approximately the same effect upon the $K_{Bas.}$ of the medium, it would appear that the basicity constants of methyl and ethyl alcohol are nearly the same, while propyl and butyl have nearly the same basic strength. The latter are much weaker than methyl and ethyl alcohol, which in turn, are weaker than water. We are considering conductivity data rather than dissociation constants, but this is permissible since it has been shown[2] that the limiting conductivities of all these acids are approximately the same.

So long as the dissolved acid does not affect the basicity constant of the medium or affects the basicities of the different solvents in the same direction and to the same extent, the dissociations of an acid in different solvents will stand in the same ratio to one another as the basicity constants of the solvents stand to one another, regardless of the nature of the acid. This is true, provided that the solvents do not alter in any way the acidity constant of the acid; that is, the tendency to permit the dissociation of hydrogen ion from its carboxyl linkage must be the same in all solvents. If the acidity constant is altered to different extents or in different directions by the solvents, the dissociation ratios will vary accordingly. This effect is determined by the relative electron-sharing properties of the groups attached to the hydroxyl radical of the solvent on the one hand and those of the substituent group in the acid molecule, as well as the position of this substituent with reference to the carboxyl radical and its effect upon the oxygen to hydrogen bond, on the other.

Fig. 2 shows typical curves for the conductances of acids in acetone solutions at different dilutions. Table VI shows that propyl and butyl alcohols affect the conductivity in methyl alcohol almost equally, while the effect of propyl on the conductivity in ethyl alcohol exceeds that of butyl.

Experimental

The molecular conductances and dissociation constants of several acids in ethyl alcohol at 30°C are given in the following tables.

The limiting conductivities of the acids were computed by means of the following equation:

$$\Lambda_o\text{acid} = \Lambda_o\text{Na salt} + \Lambda_o\text{HCl} - \Lambda_o\text{NaCl}.$$

The conductivities of the sodium salts at 30°C were calculated from the work of Lloyd and Pardee.[3]

The conductivity of NaCl at infinite dilution was determined in our laboratory.

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[1] Brönsted: Chem. Reviews, 5, 308 (1928).

[2] Lloyd and Pardee: Pub. Carnegie Inst. Wash., No. 260, p. 99.

[3] Lloyd and Pardee: Pub. Carnegie Inst. Wash., No. 260, p. 99.

Dilution	Mo. Cond. 30°C.	Dilution	Mol. Cond. 30°C
400	37.6	4000	45.6
800	40.93	∞	53.675
2000	43.6		

The conductivity at infinite dilution was found by means of Kohlrausch's formula:

$$\Lambda_o = \Lambda v + (aC^{1/3}).$$

There is a pronounced disagreement in the data dealing with the conductivity of HCl at infinite dilution. Goldschmidt's[1] value is 89.4 at 25°C. This is higher than that first obtained by him (74.3) and also considerably higher than that obtained by Partington and Lapworth[2] (66.5).

Goldschmidt's value for the limiting conductivity of HCl has been calculated by use of the Kohlrausch formula. Lloyd and Pardee question this method of calculation and recalculate the value at infinite dilution from Goldschmidt's data, by using the equations of Noyes[3] and Randall.[4] Lloyd and Pardee's value for the conductivity of HCl at infinite dilution is 82. Goldschmidt has determined the limiting conductivities of the sodium salts of a few organic acids. These and others have been determined by Lloyd and Pardee. Because of differences in the methods of calculating Λ_o, Goldschmidt's values are uniformly about 10 reciprocal ohms higher than those of Lloyd and Pardee.

Partington[5] has measured the limiting conductivity of HCl in ethyl alcohol at 0°, 18°, and 25°C, and has found a value for the temperature-coefficient. From these data we have calculated the value of Λ_o for HCl at 30° as 72.42. Using this value for the limiting conductivity of HCl, Lloyd and Pardee's values for the sodium salts of the acids, and our own value for the limiting conductivity of NaCl, we have determined the limiting conductivities of the acids. Their dissociation constants have been calculated from the well known Ostwald equation

$$K = \alpha^2/(1 - \alpha)V.$$

Goldschmidt has calculated the dissociation constants for a few of these same acids. We find good agreement between his values and ours when we use the higher values that he gives for the limiting conductivities of HCl and the sodium salts. Since there are such great discrepancies in the observations of the limiting conductivity of HCl and the sodium salts of certain organic acids, the authors propose to check these values as soon as possible. In the meantime we have used Partington's value for HCl as the only one available at 30°C, and Lloyd and Pardee's data on sodium salts as these cover nearly all the cases which we have investigated. We do not claim absolute accuracy for the constants. Our dissociation constants for the various acids

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[1] Goldschmidt: Z. physik. Chem., 89, 131 (1914).

[2] Partington and Lapworth: J. Chem. Soc., 99, 1419 (1911).

[3] Noyes: J. Am. Chem. Soc., 30, 335 (1908).

[4] Randall: J. Am. Chem. Soc., 38, 788 (1916).

[5] Partington: J. Chem. Soc., 99, 1937 (1911).

are only relative, but they enable us to compare the acids on the basis of the effect of substituent groups upon the dissociation of hydrogen from its carboxyl linkage. The dissociation constants obtained for a few acids by Goldschmidt were calculated from molecular conductivity data in solutions in which the dilution ranged from about 10–20 liters. The constants which we are quoting herewith are obtained from molecular conductivity data at dilutions of 8, 32, 128, 512, and 1024 liters. It will be noted that these values, in general, seem to decrease as the dilution increases to what would eventually prove a constant value in very dilute solutions. There is, however, no evidence of constant values over the wide range of dilution at which we have calculated the dissociation constants.

TABLE VIII

Dilution	o-Nitrobenzoic	m-Nitrobenzoic	p-Nitrobenzoic	o-Toluic	m-Toluic	p-Toluic
2	0.0594	0.0718		0.0098	0.0772	
8	0.0951	0.0942	0.0569	0.0133	0.1231	0.0107
32	0.1515	0.1239	0.0741	0.0234	0.2479	0.0223
128	0.2952	0.1836	0.1228	0.0442	0.3431	0.0383
512	0.4928	0.3397	0.2393	0.1273	0.4852	0.1098
1024	0.7019	0.4751	0.3177	0.1502	0.5564	0.1520

Sp. Cond. of alcohol 1.61×10^{-7}

TABLE IX

Dilution	o-Chlorobenzoic	m-Chlorobenzoic	p-Chlorobenzoic	o-Aminobenzoic	m-Aminobenzoic	p-Aminobenzoic
2	0.0208			0.0713		0.0277
8	0.0317	0.3485	0.0115	0.1036		0.0374
32	0.0604	0.4388	0.0219	0.1307	0.1070	0.0421
128	0.1006	0.4919	0.0606	0.1989	0.1754	0.0568
512	0.2225	0.5688	0.1475	0.4530	0.2207	0.0957
1024	0.4792	0.6319	0.2141	0.7629	0.2510	0.1270

Sp. Cond. of alcohol 145×10^{-9}

TABLE X

Dilution	o-Hydroxybenzoic	m-Hydroxybenzoic	p-Hydroxybenzoic	Benzoic	Phthalic
2	0.0123	0.0131		0.0018	
8	0.0299	0.0190	0.1352	0.0045	0.0591
32	0.0488	0.0285	0.1408	0.0110	0.1235
128	0.1079	0.0673	0.1833	0.0376	0.2553
512	0.2690	0.1709	0.3975	0.0912	0.5394
1024	0.4149	0.2473	0.5222	0.1519	0.8211

Sp. Cond. of alcohol 200×10^{-9}

TABLE XI

Dilution	Succinic	Malonic	Oxalic	Fumaric	Maleic	Adipic
2		0.0386	0.2016		0.2658	
8	0.0123	0.0576	0.3939	0.0253	0.5145	0.0050
32	0.0239	0.0905	0.6459	0.0515	1.0185	0.0138
128	0.0528	0.1672	1.1630	0.1655	1.9814	0.0474
512	0.1153	0.3229	2.9489	0.2516	3.7961	0.1249
1024	0.2027		4.2390	0.3127	5.2205	0.1858

Sp. Cond. of alcohol 196×10^{-9}

TABLE XII

Dilution	Meso-Tartaric	Dextro-Tartaric	Crotonic
2			0.0044
8	0.3727	0.0221	0.0104
32	0.7344	0.0448	0.0189
128	0.9811	0.0912	0.0425
512	1.1045	0.2308	0.1089
1024	1.1415	0.3158	0.1538

Dissociation Constants

Note: All values recorded below are to be multiplied by 10^{-8}, except values for the conductivity of the acids at infinite dilution.

TABLE XIII

Dilution	o-Nitrobenzoic	m-Nitrobenzoic	p-Nitrobenzoic	o-Toluic	m-Toluic	p-Toluic
8	30.8	30.8	9.6	0.66	56.7	0.43
32	19.7	13.3	4.5	0.51	57.8	0.47
128	18.7	7.3	3.1	0.45	27.7	0.34
512	13.0	6.3	3.0	0.94	13.8	0.71
1024	13.1	6.1	2.6	0.66	9.1	0.69
Λ_0 of acid	60.3	59.8	61.2	57.67	57.6	57.3

TABLE XIV

Dilution	o-Chlorobenzoic	m-Chlorobenzoic	p-Chlorobenzoic	o-Aminobenzoic	p-Aminobenzoic
8	3.1	417.0	0.45	39.0	5.4
32	3.1	165.0	0.42	15.7	1.7
128	2.2	51.2	0.8	9.2	0.78
512	2.7	17.4	1.17	11.7	0.55
1024	6.2	10.5	1.24	16.5	0.48
Λ_0 of acid	60.2	60.26	60.0	58.33	56.7

TABLE XV

Dilution	o-Hydroxy-benzoic	m-Hydroxy-benzoic	p-Hydroxy-benzoic	Benzoic
8	1.6	13.6	73.2	0.075
32	1.9	0.7	19.8	0.107
128	2.3	1.0	8.4	0.312
512	3.6	1.71	9.9	0.459
1024	4.3	1.8	8.5	0.64
Λ_0 of acid	62.4	57.6	55.8	59.5

Discussion of Results

The structure of benzene and its derivatives, from the viewpoint of the electronic theory of valence, is well summarized by the concepts advanced by Huggins[1] and Crocker.[2] Huggins favors a structure of benzene in which the carbon atoms, with the bonds which tie them to hydrogen or other atoms or radicals, are in two parallel planes, each of which contains three carbon atoms. There is much evidence in favor of this view in the results that have been obtained by the analysis of X-ray measurements of benzene derivatives and by absorption spectra studies. Recently MacInnes[3] has found evidence to support this view, which is essentially that of the Körner centroid structure for benzene, in his study of the ionization constants of the halogen and methyl substituted benzoic acids in water solutions. MacInnes finds the relative values for the dissociation constants of these acids, when the second substituent is in the ortho, meta, and para position with reference to the carboxyl group, agree with the spatial requirements of the Huggins structure. The hydroxyl acids agree only fairly well with this relation, however, and the nitro-benzoic series furnishes complete exception. An attempt to apply MacInnes' methods of calculation and graphical representation to the dissociation constants of these acids in alcoholic solutions does not lead to any conclusive results.

Crocker's theory of the electronic configuration of the benzene molecule has proved helpful in reconciling the views of many investigators who have made suggestions concerning structure and orientation in benzene derivatives. Berliner[4] has recently summarized Crocker's theory and has used it in interpreting his studies of association and vapor pressure measurements of the nitroanilines, mononitrotoluenes, and toluidines.

Crocker distributes the electrons in the benzene molecule as follows. Each of the six carbon atoms in the benzene ring is attached to the two adjacent carbon atoms and to its hydrogen atom by a pair of electrons. This accounts for twenty-four of the thirty valence electrons possessed by the six

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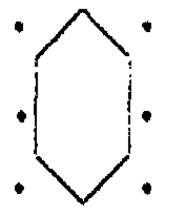
[1] Huggins: Science, 55, 674 (1922); J. Am. Chem Soc., 44, 1607 (1922); 45, 264 (1923).

[2] Crocker: J. Am. Chem. Soc., 44, 1618 (1922).

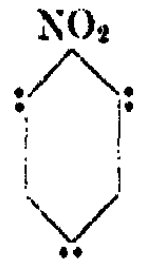
[3] MacInnes: J. Am. Chem. Soc., 50, 2587 (1928).

[4] Berliner: J. Phys. Chem., 32, 307 (1928).

carbon and six hydrogen atoms. The remaining six electrons are placed between the carbons and in the plane of the ring, as shown:



If an ortho or para orienting group replaces hydrogen, these six electrons, which are referred to as the "aromatic" electrons, are attracted toward the 1, 3, and 5 positions and repelled at the 2, 4 , and 6 positions. If the substituent orients in the meta position the electrons are attracted towards the 2, 4, and 6 positions and repelled at positions 1, 3, and 5.



The carboxyl group is meta orienting, and so in the molecule of benzoic acid we may expect to have the six aromatic electrons grouped in pairs at the 2, 4 and 6 positions. Thus, we may say, that the carboxyl substitution tends to make the carbon atom in position one more electro-positive and the carbon atom in position two more electro-negative by the shift that its introduction into the molecule produces in the arrangement of the aromatic electrons. The change is one in the degree of polarity between the carbon atoms of the ring. This effect will be noticed in the rate and extent of substitution of various atoms or radicals for the hydrogen attached to different carbon atoms, and the polarity of the ring and carboxyl carbons will, in turn, be influenced by the character of the substituent which replaces hydrogen.

If an atom of chlorine or any other substituent, which strongly attracts the paired electrons between itself and carbon, is substituted in the ortho position to the carboxyl, the carbon atom to which it is attached becomes less electro-negative in character because of the attraction of the chlorine nucleus and the consequent displacement of the pair of electrons away from the ortho carbon atom. Stieglitz[1] makes this carbon altogether positive. This view agrees with the shift in electrons in unsaturated hydrocarbons. Kharasch[2] and others have developed the conception that in vinyl chloride and similar structures the bonding electrons are shifted away from the carbon atom to which chlorine is attached, causing the adjacent carbon atom to assume a relatively electro-negative character. Upon the substitution of chlorine in the ortho position, therefore, the carbon atom to which the carboxyl group is attached becomes more negative and the carboxyl carbon more positive. The opposite effect is produced when chlorine is attached

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[1] Stieglitz: J. Am. Chem. Soc., 44, 1293 (1922).

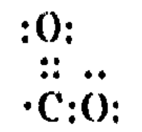
[2] Kharasch: Chem. Reviews, 5, 511 (1928).

to the carbon atom in the meta position with reference to the carboxyl group. These differences in polarity, although only slight, should cause at least a noticeable difference in the dissociation of the hydrogen from the carboxyl. Meta-chlorobenzoic acid should be more strongly dissociated than ortho-chlorobenzoic acid. If this were true, it would seem to bring into partial agreement the views of Stieglitz, Lewis,[1] Kharasch, and others.

Lewis' contention that chlorine causes a shift of the electrons about the nuclei of all the intervening atoms in the same direction, regardless of the presence of unsaturation ("aromatic" electrons), is not consistent with this idea, however. So far as his theory is applied within the carboxyl group itself, there is agreement. In view of the data supplied by the chemical reactions of halogen acids with the chlorine derivatives of unsaturated compounds, it is believed that we must come to the conclusion, contrary to Lewis, that chlorine substitution results in the production of an electro-negative condition for the carbon atom opposite that to which chlorine is attached.

Meta-chlorobenzoic acid is not stronger than the ortho derivative in water solutions. Lewis calls attention to the fact that the dissociation constants for the chlorobenzoic acids are: ortho, 1.3×10^{-3}; meta, 1.6×10^{-4}. He uses this as an argument against the views of Stieglitz, who assumed that chlorine makes the carbon, to which it is attached, positive. Kharasch argues that the halogen benzoic acids should be only slightly more dissociated than benzoic acid, since, even in the ortho position, the halogen is on the beta carbon atom, and in the aliphatic acids the effect of a halogen on a beta carbon is very slight. He notes that the effects in the aromatic acids are of the same order as that produced when the halogen is substituted on the alpha carbon in the aliphatic acids. But here and in his statements concerning the toluic acids, he disregards the six aromatic electrons, the unsaturation of the benzene ring, and the fact that a substituent produces a change in the electro-positive and electro-negative conditions of the various carbon atoms of the ring and of the carboxyl.

Kharasch also finds the fact, that formic is a stronger acid than benzoic, an argument aginst Lewis' statement that "methyl alcohol is a weaker acid than water, phenol is a stronger acid." In this case he disregards the fact that in benzoic acid, hydrogen is attached to the phenyl group through the carbon atom of the carboxyl and that in phenol the hydroxyl group is attached directly to the phenyl group. If the phenyl group is more electro-negative than hydrogen, phenol should be a stronger acid than water, ($C_6H_5O^-H^+$); and again if phenyl is more negative than hydrogen, the



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group is more positive in benzoic acid than in formic, and benzoic acid should therefore be weaker. That the electro-negativity of the phenyl group does

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[1] Lewis: "Valence and the Structure of Atoms and Molecules," 142-146.

produce such an effect upon the carbon atom of the carboxyl, and even in a chain attached to it, is evidenced by the fact that the carboxyl group is meta orienting, while the CH_2COOH group, in which the carboxyl is attached to the ring by a carbon atom twice removed, is ortho and para orienting. Lewis has pointed out this fact in support of Flürscheim's[1] alternation of "residual affinity" within the ring and in the attached carbon chain. The views which we express have much in common with Flürscheim's hypothesis.

Kharasch goes on to state that "the only conclusion that one may draw from these data (ionization constants) is that ionization is a molecular effect, and that in our imperfect knowledge of the effect of the solvent in causing ionization . . . that it is not permissible to draw conclusions in regard to the electro-negativity of organic radicals from these premises." In this statement we thoroughly agree with Kharasch and are herewith presenting dissociation data in ethyl alcohol solutions in order that these views may be tested in some solvent other than water. We believe that water is not a suitable solvent in which to compare the dissociation of organic acids as regards the electro-negativity of the radicals, induced polarities, inner salt formation, or any other property which may depend in whole or in part upon the presence of polarity, wholly or partially within the acid molecule. The electrical moment of the water molecule and its hydrogen-accepting properties (basicity) is so great that any phenomenon which depends upon the presence of minor degrees of polarity and hydrogen-accepting properties within the acid molecule or its substituent groups is almost completely overshadowed by the effects due to the stronger influence of the water molecule.

Brönsted[2] has shown from the data of Larsson[3] and Michaelis and Mizutani[4] that ethyl alcohol is about 600 times as weak a base as water. Brönsted has pointed out the significance of the basicity of the solvent in determining the true acidity constant of the acid from its dissociation constant. In ethyl alcohol solutions, where the hydrogen of the carboxyl is permitted more completely to display its natural dissociation tendency in the presence of a solvent whose molecules are not so highly polarized, and in which the oxygen atom of the hydroxyl group is not an extremely strong "donor," the meta-chlorobenzoic acid is much stronger than the ortho derivative. Para is slightly weaker than the ortho-chlorobenzoic acid, as might be expected, because of the greater distance in this case between the carbon atoms to which the chlorine atom and the carboxyl group are attached. This also holds true for the ortho, para, and meta toluic acids. Meta toluic acid is decidedly stronger in alcoholic solutions than either the ortho or para isomer, and of the two, ortho is slightly stronger than para. This is in agreement with the electronic configuration of the benzene molecule which has been discussed earlier in this paper. We are not comparing the electronegative character of methyl to hydrogen, but rather the effect of the same

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[1] Flürscheim: J. prakt. Chem., (2), 66, 321 (1902); 71, 497 (1905).

[2] Brönsted: Chem. Reviews, 5, 231 (1928).

[3] Larsson: Dissertation, Lund (1924).

[4] Michaelis and Mizutani: Z. physik. Chem., 116, 135 (1925).

group, CH_3, in two different positions with reference to the carboxyl. Crocker considers the methyl group as acting in much the same manner as the chlorine atom, because of the strong nuclear positive charges on the carbon atom and the three hydrogen nuclei attached to it.

The results for the hydroxyl, amino, and nitro-benzoic acids are not so clear cut as we have found them to be in the series of chlorine and methyl substituted benzoic acids. Meta-hydroxy-benzoic acid is decidedly weaker than the para, but stronger than the ortho derivative. We must remember that in both the hydroxyl and amino groups the oxygen and nitrogen atoms respectively have strong hydrogen accepting properties. It is the hydroxyl group that gives water and alcohol their basic properties; it is the amino group that so decidedly decreases the dissociation of the acid when NH_2 replaces a hydrogen in the methyl group of acetic acid. The presence of these atoms, possessing, as oxygen and nitrogen do, free pairs of electrons to which hydrogen ion may become attached in the same manner as it does in forming $(H_3O)^+$ and $(C_2H_5OH_2)^+$, must certainly affect the dissociation of the acid in a marked manner. And it is only logical to assume that the hydrogen-accepting properties of these groups is influenced by their position on the ring.

When the amino group occurs in the ortho position to the carboxyl, there is less tendency for it to combine with hydrogen through the free electron pair on the nitrogen atom than when the NH_2 is in the meta position. This is due to the fact that the ortho carbon is relatively electro-negative while the meta carbon is electro-positive. When the amino group is attached to the ortho carbon there is less tendency for the nitrogen atom to accept hydrogen; that is, it is less negative. When in the meta position, the nitrogen atom is more negative and hydrogen is accepted more freely. This effect causes the meta derivative to be weaker, as shown by dissociation data, than it would be if the NH_2 group had no hydrogen-accepting properties, and operates in a direction opposite to the ortho and para orienting effect of the amino group upon the arrangement of the aromatic electrons and the polarity of the carbon atoms in the ring and in the carboxyl group. The same is true for the hydroxyl derivatives. This explanation agrees with the dissociation data in alcoholic solutions. In each case, the meta derivative is not as strongly, and the ortho is more strongly, dissociated than one would be led to expect from comparison with the relative values of the two chloro and two methyl derivatives. There are no free pairs of electrons (unsaturated bonds) attached to the carbon atom of the methyl group; while in the case of the strongly negative chlorine atom, although it possesses three free pairs of electrons, there is no indication of its tendency to accept hydrogen. For instance, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$ is highly ionized, perhaps 100%.

It is of interest to note in this connection that MacInnes[1] has found the chloro and methyl benzoic acids to be the only derivatives that regularly fall into accord with his graphical representation of their dissociation con-

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[1] MacInnes: J. Am. Chem. Soc., 50, 2587 (1928).

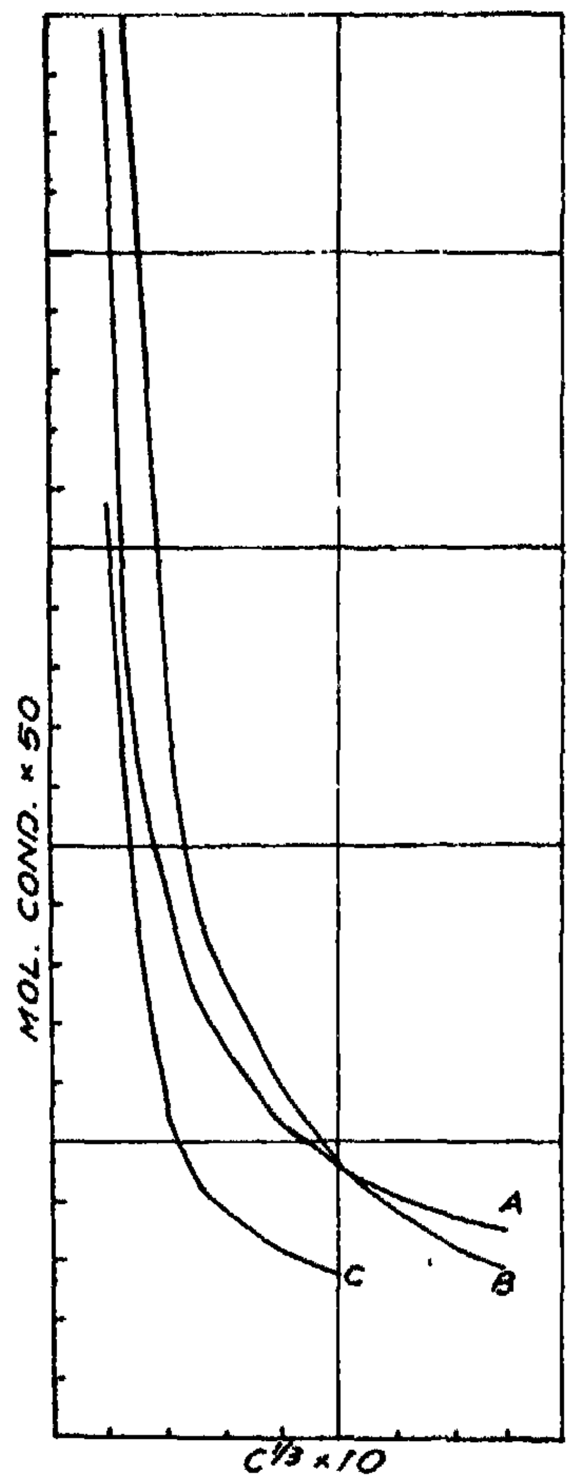


Fig. 3
A. m-nitrobenzoic Acid
B. o-nitrobenzoic Acid
C. p-nitrobenzoic Acid

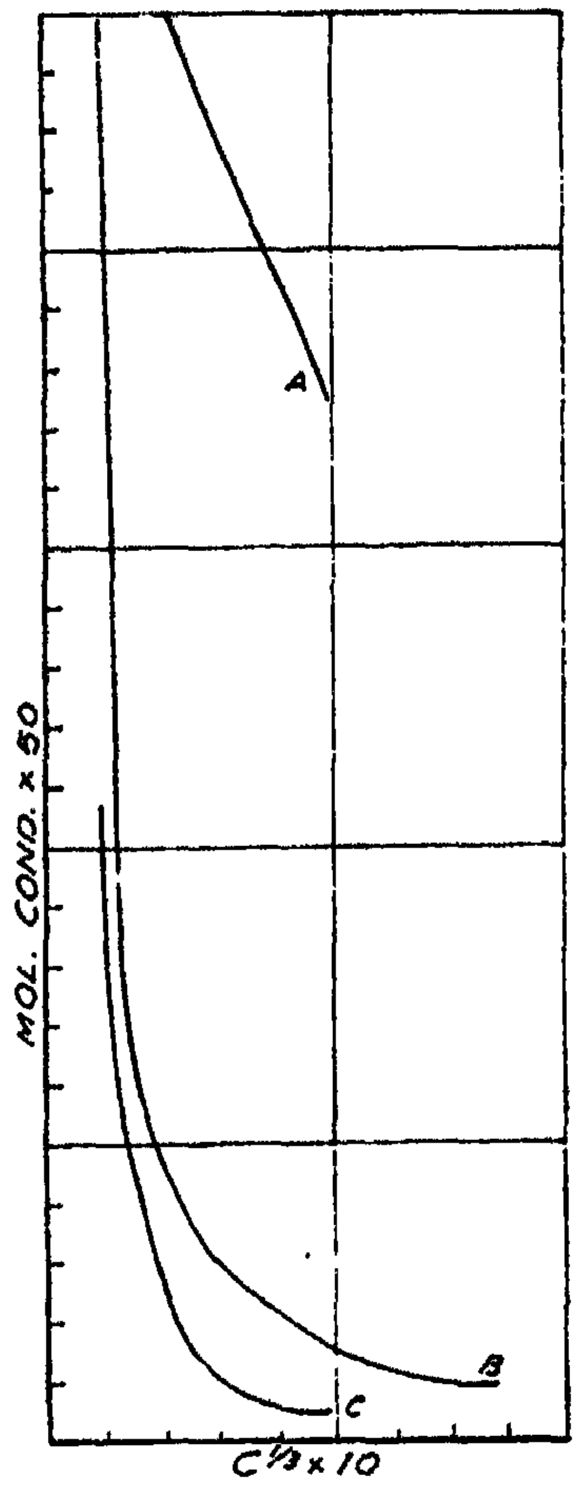
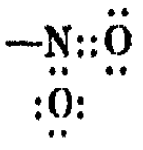


Fig. 4
A. m-chlorobenzoic Acid
B. o-chlorobenzoic Acid
C. p-chlorobenzoic Acid

stants and the relative distances that separate them from the carbon atom to which the carboxyl group is attached in accordance with Huggins' conception of the electronic configuration of the benzene molecule and its derivatives.

Ortho-nitrobenzoic acid is slightly more dissociated in alcoholic solution than the meta derivative. In the nitro group there is no single atom possessing a nuclear charge sufficiently effective to overcome the repulsive effect of the free electron pairs about the nitrogen and oxygen atoms. The bonding electron pair between carbon and nitrogen, therefore, may be repelled rather than attracted as in the case of chlorine. Meta-nitrobenzoic acid should be weaker, therefore, than the ortho isomer, for the same reason that the meta form is stronger than the ortho in the chlorobenzoic acid series. Furthermore, the structure of the nitro group is probably



$$\begin{array}{l}-\underset{\cdot\cdot}{\mathrm{N}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\\ :\underset{\cdot\cdot}{\mathrm{O}}:\end{array}$$

as shown by Sidgwick.[1] Here the nitrogen atom shares a complete pair of its own valence electrons with oxygen to form a coordinate bond. This results in a slight degree of polarity in which the nitrogen atom becomes slightly more electro-positive. The effect upon the carbon atom to which it is attached is to make that atom slightly more negative, and if this carbon is in the ortho position with reference to the carboxyl group, the acid should be more strongly dissociated than if the nitro group is in the meta position.

The presence of unshared pairs of electrons about the atoms that compose the substituent group should have an effect upon the attraction of the substituent for the bonding pair of electrons between it and the carbon atom in the ring. This effect should influence polarity within the ring and also in attached chains. That such is the case may be seen from the fact that the percent of increase in conductivity (over that of benzoic acid) is almost directly proportional to the number of unshared electrons about the various atoms that constitute the substituent. To obtain this result the conductances of the ortho, para, and meta members of each series must be averaged. When considered individually, successive changes from a group possessing no free electrons (CH_3) to one possessing two (NH_2), then four (OH), then six (Cl), and finally ten (NO_2) show an opposite effect when the substituent is placed on the ortho atom to that obtained when it is in the meta position. The effect in the para position is smaller than that produced when the substituent is in the ortho position with reference to the carboxyl group.

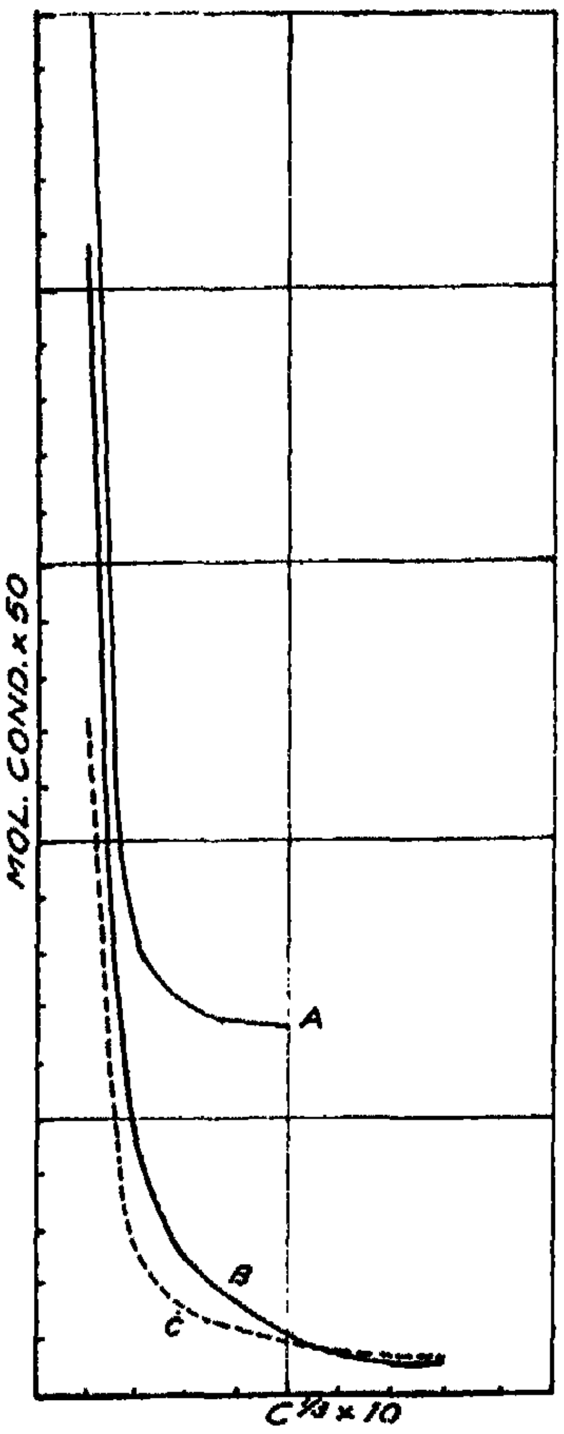


Fig. 5

A. p-hydroxybenzoic Acid
B. o-hydroxybenzoic Acid
C. m-hydroxybenzoic Acid

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[1] Sidgwick: "The Electron Theory of Valence," 65.

The following additional facts may be noted concerning the relative values of the conductivity of various acids in alcoholic solutions. The conductance of dibasic acids decreases as the number of CH_2 groups separating the carboxyl groups increases.

In maleic and fumaric acids, the cis-acid is about ten times stronger than the trans-acid. These relations are the same in water solutions.

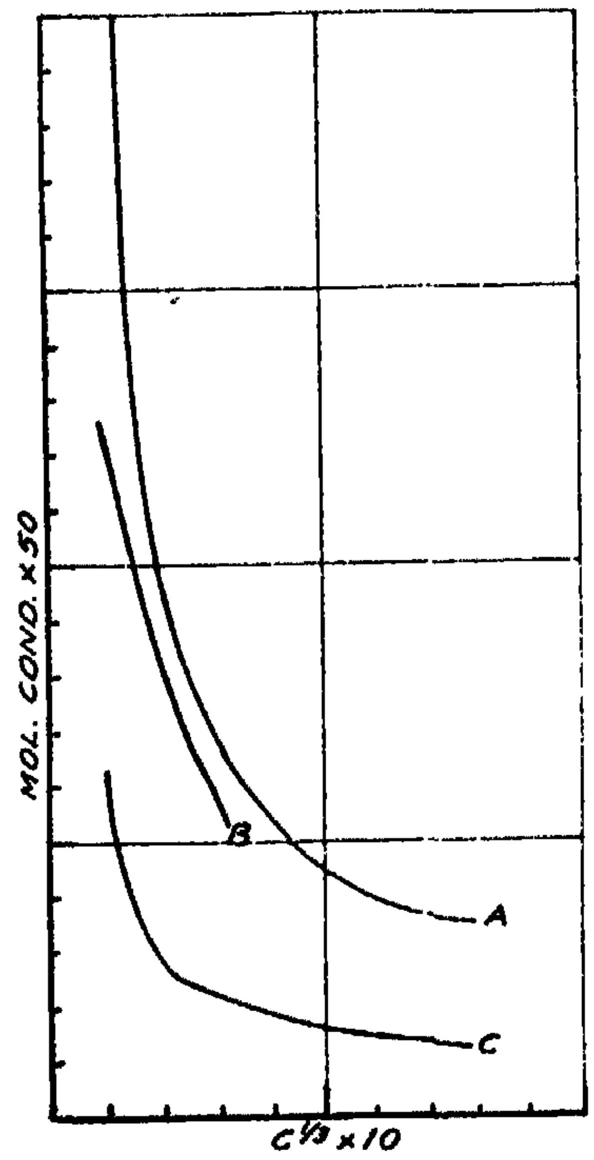

Fig. 6

A. o-aminobenzoic Acid
B. m-aminobenzoic Acid
C. p-aminobenzoic Acid

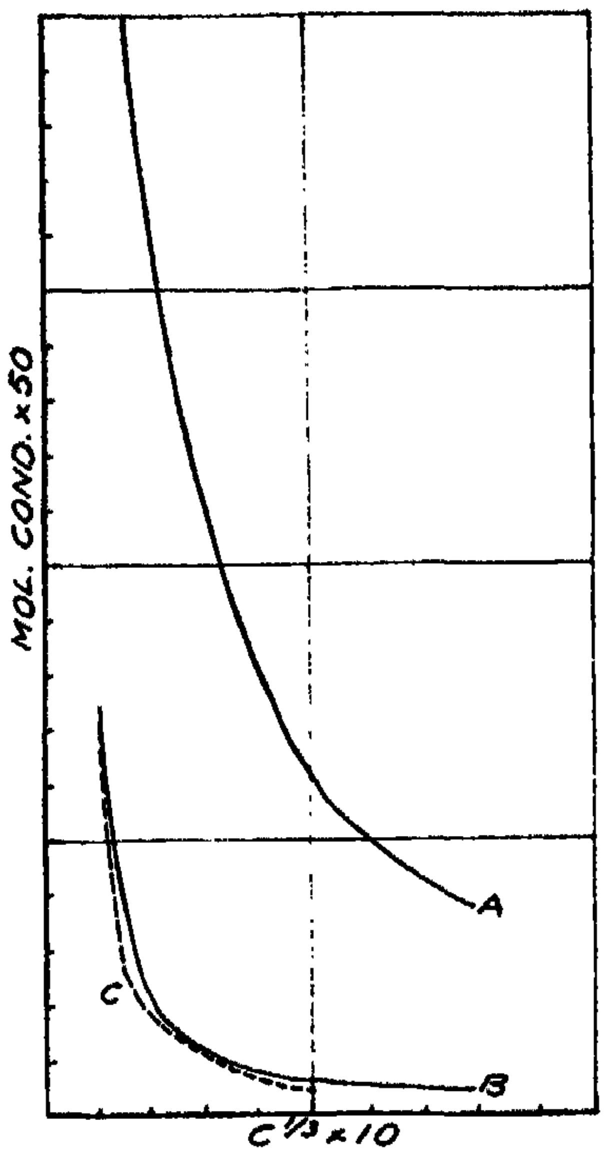

Fig. 7

A. m-toluic Acid
B. o-toluic Acid
C. p-toluic Acid

The effect of the double bond upon the dissociation of the hydrogen atom in the carboxyl is illustrated in crotonic acid. Crotonic acid is from four to five times weaker than butyric acid, as shown by conductivity data in alcoholic solutions. This leads to the conclusion that there is at least a slight degree of polarity between the doubly bonded carbon atoms, and since the carboxyl carbon atom in crotonic acid is evidently more electro-negative than that in butyric acid, we may assume that, in crotonic acid, the alpha carbon atom is electronegative and the beta carbon atom is relatively electropositive. This agrees with the fact that crotonic acid yields beta-bromobutyric acid upon treatment with HBr, while butyric acid reacts with bromine to form the alpha derivative.

Figs. 3, 4, 5, 6, and 7 show curves for the molecular conductivities against the cube root of the concentration of the different series of substituted benzoic acids.

Summary

The conductances of various organic acids in methyl, ethyl, propyl, and butyl alcohol and acetone have been measured at 30°C.

The conductances of substituted benzoic acids, and a few unsaturated and dibasic acids have been measured in ethyl alcohol.

The results have been interpreted in terms of the electron theory of valence and current theories of molecular structure.

THE ALLEGED CATALYTIC ACTION OF FULLERS EARTH ON COLORING MATTER IN OILS

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BY J. D. HASEMAN

Some writers have maintained that bleaching with fullers earth is a chemical process, others that it is a physical process, and still others that it is both chemical and physical action. Some have maintained that fullers earth contains an unknown substance which combines with the coloring matter, rendering it insoluble; others that the bleaching is associated with the colloidal silica contained in fullers earth; others that fullers earth polymerizes the color compounds; others that fullers earth dialyzes the color from the oil; and most of the writers that it is due to selective adsorption. They have agreed that the bleaching of fullers earth is in some way associated with its porosity.

There are equally diverse ideas and views in regard to the nature of the coloring matter in oils, especially the nitrogen-compound coloring matter. Some writers claim that this coloring matter is related to the pyridine compounds; and others maintain that the coloring matters are oleosols of high molecular weights.

The purpose of this paper is to prove that fullers earth does not bleach by a mysterious catalytic power or selective adsorption which is in some unknown way associated with its porosity; but that fullers earth contains solid or pectoid di-silicic acid or its anhydride which precipitates the color compounds that contain nitrogen, and that these color compounds are humic acids more or less affected by the heat, acid, and alkali treatment of oils.

The Origin of Fullers Earth

It has generally been conceded that the original source of the sedimentary material, which has been transferred into fullers earth, was such basic rocks as hornblende, augite, etc.; but it more probably came from rock-making silicates that form colloidal solutions when boiled with acid, such as nephelite, sodalite, analcite, olivine, chondrodite, serpentine, anorthite, leucite, noselite, stibilite, heulandite and cancrinite, (mostly anorthite).

The location of good deposits of fullers earth in the United States show, when the general geology is taken into consideration, that they were deposited parallel to the ancient shore lines at some distance out in relatively shallow seas and bays whose beds were sometimes sinking and sometimes rising due to the general continental subsidences and elevations.

As a result of these oscillatory movements of the ancient shore lines and changes in the direction of currents carrying clastic sediments, both lime and sand were, from time to time, mixed in the clay sediments, and at times pure clay, sand and lime were laid down. The deposits now known as fullers earth were formerly nothing more than peculiar calcareous clays or clay-like compounds, having pyrite and marcasite in or near them, and having little or no bleaching properties.

The deposits destined to be fullers earth were not pure aluminum silicate types of clays even though they contained iron, calcium, magnesium, potassium, sodium, titanium, phosphorus, and sulphur similar to that now found in most lacustrine and marine clays; because clays cannot be readily turned into good fullers earth. These deposits that were destined to become fullers earth had considerable aluminum hydroxide mixed in the clay as well as colloidal pectoid silica.

When the major continental oscillations were concluded and the coastal plains were left more or less as we now find them, incessant surface and subsurface erosion have materially changed the nature of the beds of clays in the region of the present and past underground water levels.

The coastal plains of the United States where good beds of fullers earth are found are not only sandy but also more or less swampy. This condition has a bearing on the production of good bleaching fullers earth.

Sand is slightly soluble in water. It is more soluble in certain humic acids. Azo-humic acids, formed only or at least in far greater quantities in swampy regions where sand is in preponderance to clay, dissolve sand, forming azo-silico-humic acids. These dark-brown humic acid water swamps are or have been prevalent throughout the coastal plains and are or have been associated with the activation of good bleaching fullers earths; because of the production of azo-silico-humic acids and carbon dioxide.

The beds of fullers earth found on high hills and stream bluffs are more or less changed locally into flint, opalized and agatized sand, and even into pure siliceous rock resembling glass somewhat. The aluminum content has been removed and replaced by silica. Such beds are more or less exposed and above the present underground water level. This type of fullers earth is no good for bleaching.

The deposits of fullers earths with relatively little overburden and in regions of the existing underground water level are invariably the best bleaching earths. Often when a good bed of fullers earth is mined back into high hills, that are composed of the original deposits, the bed becomes no good for bleaching. This is due to the fact that the underground water level is higher because of impervious hardpans nearer the surface of the high hills and consequently the surface swamp waters charged with azo-silico-humic acids and carbon dioxide do not affect the deposits. Likewise the marcasite and pyrite did not turn into sulphuric acid and do its part of the activation. The sulphuric acid not only affects the lime content a little but it dissolves out the aluminum which is in the form of a hydrate. This latter has more to do with the formation of porosity than does the loss of lime as has hitherto been maintained. The Alum Bluff Formation gets its name due to alum found in it and it is this series that yields the Florida type of fullers earth. The swamp waters carrying silica in solution then deposit colloidal silica in the clays and the activation is complete.

The deposits of fullers earth found below the present underground water levels are also no good for bleaching because they have not been activated. When some of the lime and aluminum contents of such clays are removed by acids, they will then bleach fairly well; and if colloidal silica be added by precipitating it properly in this acid-treated earth, it will be good bleaching earth.

Hence even though the chemical analyses do not reveal much difference between good and poor bleaching fullers earths, there are very important geo-chemical differences. The silicon content of the high and dry deposits is much in the form of a true silicon dioxide. The silicon content of the deposits below the underground water is much in a pectoid state but inactive because of the excess of aluminum hydroxide which must mostly be removed as alum before the solid acid can precipitate color compounds.

The same is true in the case of activating bentonite, halloysite, indianaite, etc. In the case of bentonite one can use about one-third of its weight of commercial sulphuric acid diluted in two thirds it weight of water and boil gently about three hours to remove most but not all of its aluminum content as alum. In the case of halloysite it takes more than its weight of acid because it contains more than three times the aluminum content that bentonite has. Indianaite has about twice the aluminum content that bentonite has. Hence to leave about the same amount of aluminum in it, it will take not quite its own weight of acid. Indianaite has been called kaolin but it is not. When pure it has about 40% silicon dioxide content, 40% aluminum oxide content and 15% combined water and the rest free water and traces of iron, etc. This clay is in reality aluminum hydroxide and di-silicic acid. To activate it, one has only to remove most but not all of the aluminum. About 5 or 6 percent of the aluminum in some way facilitates the di-silicic acid in freeing H and OH ions used in bleaching neutral oils; but sulpho acid colors bleach best with little or no aluminum content in the clay.

Hence even though fullers earth has generally been considered to be hydrous aluminum silicate it is not. It does contain combined aluminum and silicon but it is not this portion that does the bleaching. American fullers earths usually have 8 to 10% combined water; consequently the active part cannot be either smectite or malthacite as suggested by some authorities because these minerals contain around 30% combined water. Fullers earth rarely bleaches well unless it contains five times as much silicon content as aluminum. Part of this silicon content is pure silicon dioxide and part is a true aluminum silicate, but the active part is di-silicic acid.

The fact that the activation of indianaite, bentonite, halloysite, etc., require just the right strength of acid, amount of acid, temperature and time to produce the most efficient bleaching compound, also explains why some fullers earths bleach better than others. The natural process of activation is more complete or perfect in some places than others and some beds have less inert materials in them.

The Nature of the Coloring Matter in Oils

In a paper entitled the humic acid origin of asphalt published by the bulletin of the American Association of Petroleum Geologists, I pointed out that asphalt had been made from humic acid on our gulf coast since America was discovered. Since then I have done considerable experimental work on a fossil humic acid commercially known as vandyke brown.

Vandyke brown is an azo-humic acid containing 57% carbon of which 45% is fixed, 33% oxygen, 7% hydrogen, and 3% nitrogen. It is only soluble in alkalies such as soda ash, caustic soda, ammonium hydroxide, etc. It then forms sodium azo-humate which is sap brown or soluble vandyke brown. When either sap brown or vandyke brown is heated in a closed retort it gives off offensive odors quite like some of the crude oil refining odors. Concentrated sulphuric acid will carbonize van dyke brown, also yielding offensive odors similar to those when it is added to crude oil. Vandyke brown lakes with oil, making a transparent brown paint. Sap brown is precipitated by any weak acid or acid salts and vandyke brown is formed again.

When a warm concentrated colloidal solution of sap brown is treated with a large excess of concentrated sulphuric acid, the vandyke color in part breaks up into acid red and yellow colors if water is added to dilute the acid. The red will filter off first and as more water is added the color then turns to yellow. These red and yellow colors are, as far as I was able to discern, exactly like red and yellow colors extracted from fullers earth oil cake. They are evidently complicated sulpho-compounds of azo-humic acid. During the formation of the red and yellow colors, fixed carbon, carbon compounds, sulphur dioxide, gases, and offensive odors were also produced.

I have burned fullers earth cake mildly in the air and extracted alkali from it. In this state the cake will readily yield a yellow color to gasolene when leached with it. The cake can then be treated with caustic soda in a slight excess so as to saponify the remaining free oil and obtain a red color. Fullers earth will precipitate these red and yellow colors as it does the same colors obtained from sap brown. It readily precipitates the red but leaves a little of the yellow color. The above acid red and yellow colors are readily precipitated by calcium oxide. Lime will also precipitate some of the coloring matter in oils.

Cotton and mineral oils are first treated with sulphuric acid. Weak sulphuric acid will precipitate any free sap brown like-color material laked in oil. Stronger sulphuric acid will precipitate some vandyke brown as carbon compounds which yield also some red and yellow acid colors. These colors combine with caustic soda in part that is then added to neutralize the sulphuric acid before the oil is bleached. Concentrated sulphuric acid will redden 410 neutral lubricating oil that has been bleached but still containing only a little yellow color. Lime will readily precipitate this color.

Hence some of the red and yellow colors in oils are evidently made by breaking down azo-humic acids with sulphuric acid. Some are broken down by heat and some are yet in their natural state, i.e. are not yet oxidized into the vandyke-like state. Vandyke is readily precipitated but the red and yellow colors are not as readily precipitated.

The acid red and yellow colors obtained from sap brown yield a small precipitate similar to mineral oils left for some time exposed to sunlight. Vandyke brown slowly darkens when exposed to sunlight for a long time. The color compounds in cotton oil sludges can readily be oxidized by strong sulphuric acid into a tar resembling asphalt.

The Nature of Fullers Earth's Action on Color Compounds

1. *Relative acidity of fullers earth.*

All pure good bleaching fullers earths invariably show a relative acidity when mixed in distilled water and tested with phenolphthalein as an indicator. This acidity is due to free H ions; but when water is filtered from the fullers earth, it no longer shows any acidity. Hence the H ions evidently recombine with the OH ions.

It is generally agreed that pure fullers earth in some way holds OH ions and liberates the H ions which produce its relative acidity.

It has been reported that when pure sodium chloride is dissolved in pure water and filtered through fullers earth that the filtrate was acid to litmus. Therefore it was claimed that fullers earth adsorbed basic ions, sodium in the above case. I tested the above on pure Floridin XXF brand of fullers earth and found that it was not true. Some fullers earths have a little pyrite or marcasite which breaks down when the earth is dried and leave some free acid in the earth. Such an earth sometimes bleaches better than one containing no free acid. This is true if there is some free caustic soda left in the oil after the sulphuric acid-treated oil is neutralized by alkali. Other fullers sometimes have soluble lime and phosphates which even give the earth an alkaline reaction when tested in water. But as a rule all fullers earths high in free acids or free alkali or sulphates and calcium and magnesium carbonates and pyrite usually do not bleach oils well. They are also one chief source of color reversion in the bleached oils.

When one obtains the true relative acidity of a pure fullers earth by mixing it in pure water using phenolphthalein as an indicator and normal sodium hydroxide; and then makes up a pure ammonium azo-humate or sap brown solution of known strength and precipitates this sap brown with normal hydrochloric acid, he finds that it will take a quantity of fullers earth that will yield a relative acidity as great as the normal hydrochloric acid to precipitate the same amount of sap brown, and he also finds that the filtrate from the fullers earth bleached sap brown contains ammonium hydroxide equal to the relative acidity of fullers earth or the amount of normal hydrochloric acid used to precipitate the same amount of sap brown as bleached by the fullers earth.

Acid-alkali treated oils bleached by fullers earth behave the same as does sap brown. The H ions, producing the relative acidity of the earth, take the place of sodium in the color compounds and the liberated sodium forms sodium hydroxide and saponifies oil which also filters out in the fullers earth cake. Hence fullers earths with high relative acidity usually bleach better than those with lower relative acidity and the retention of oil is also usually higher.

When one adds various acids, alkalies, salts, etc., excepting di-silicic acid, to fullers earth, he rarely improves its bleaching power and usually lessens it and causes color reversion. Hence the bleaching power is entirely dependent on its true relative acidity.

2. *A list of bleaching materials.*

Bauxite, bog iron ore, china clay, bone black, ignited peat, activated carbons, activated clays, charcoal, lime, aluminum hydrate, silica-gel, platinum, sulphur dioxide, etc., have been used to separate and retain the dissolved solid and colloidal impurities such as coke, floc, moisture, finely divided carbon, etc. of oils by filtering through vertical cylinders or filter presses. It is self-evident that the action of the various above-mentioned materials on the alleged oleosols, oleofines, aromatic and cyclic unsaturated hydrocarbons, sulphur compounds, naphthenic acids, basic nitrogen compounds, finely divided carbon, asphaltic material, coke and floc said to be in oils and undesirable is not the same. Some of the above materials merely filter out a portion of the impurities, some like lime combine with the acid color compounds and filter out, and some like silica-gel, fullers earths, activated carbon and activated clays act as solid acids which precipitate some of the coloring matter and filter out the rest of it. The oleofines and aromatic hydrocarbons are readily removed by liquid sulphur dioxide but it does not remove the other objectionable materials. Silica-gel will remove the sulphur compounds better than most of the materials but will not bleach the other colors as well as activated clays.

3. *Porosity of fullers earth.*

Activated bentonite, halloysite, indianaite, etc., have greater specific gravity and less porosity than fullers earths and yet they will bleach twice as much lubricating oil as will the best grades of fullers earths. Their relative acidities are also about twice as high. Silica-gel containing a small percent of aluminum hydroxide mixed in it when it is made from sodium silicate by treatment with sulphuric acid will also bleach more mineral oil than fullers earths even though it has no apparent porosity. They also retain much less oil than do fullers earths. Fullers earths and activated silicon both retain more oil when ground in a fluffy state than when ground in a manner that the fine mesh material will be more compact. You can also fuse fullers earth with sodium carbonate and separate the silicon and aluminum contents and reprecipitate them properly with acid and then get a better bleach than from the original fullers earth even though there is much less porosity. Or you can partially plug up the pores of 100 mesh Floridin fullers earth by using about 3 parts of pure kaolin mixed in enough water to make a thick paste out of the fullers earth when stirred into the water. It will then yield as good if not slightly better bleach than pure fullers earth. Or you can use fullers earth to bleach all of the sap brown that it will precipitate in the pores and over the earth and then wash alkali free and dry carefully so as not to destroy the vandyke brown and such fullers earth containing as much as 3% vandyke brown will bleach as much oil as will the pure orignal fullers earth. These plugged up fullers earths will retain less oil than the original fullers earths.

Therefore porosity has nothing directly to do with bleaching. This is also proven by the fact that 100 mesh fullers earth will bleach as much oil as 200 mesh; but 100 mesh silica-gel and 100 mesh activated clays will not bleach as much as 200 mesh material. The grinding of the latter evidently destroys much of the porosity but it still bleaches better because there is exposed more and better surface while 100 mesh fullers earth is porous enough to expose as much surface as 200 mesh material. Hence porosity only exposes surface of the bleaching material and retains oil, but it does not directly have anything to do with bleaching.

4. *Selective adsorption.*

If selective adsorption is a phenomenon dependent on surface tension, i.e. on the difference in density or concentration of a liquid in films adjacent to bounding mediums and the density or concentration of the mass of the liquid; and if suspensoid particles attract ions of opposite electrical charge and hold them so when the colloid is precipitated, the ions are carried down also; and if this holding is not electronic chemical union but condensation at the surface of contact, then fullers earth's bleaching is not selective or any other kind of adsorption.

Fullers earth does not hold the basic ions of bleached sap brown as they (sodium and ammonia) filter through into the filtrate. The fullers earth, that is spent bleaching sap brown, will, when washed alkali free and dried at low temperature (not above 400° Fahr.), then bleach as much as the original earth. Hence the coloring matter is not held by the fullers earth by some mysterious power. The sap brown is precipitated as vandyke brown which can be dissolved from the fullers earth by caustic soda and make sap brown again. Hence the H ions liberated by the relative acidity of fullers earth replaces sodium of the sap brown and sodium hydroxide filters out while vandyke brown is precipitated the same as when weak acids are put into solutions of sap brown.

Exactly the same reaction takes place with the color compounds in oils when bleached with fullers earths. The sodium hydroxide liberated saponifies some of the oil. If this sodium liberated from the color compounds could be taken care of or if something else could be used in the place of sodium hydroxide to neutralize the acid following the acid treatment of oils, much soap stocks and retained oil could be saved.

5. *Size of the mesh of fullers earth.*

Theoretically, the size of the mesh of fullers earth has nothing directly to do with bleaching. Proper agitation and percolation can be made to produce the same results, i.e. if the H ions of the relative acidity of fullers earth are all spent. In practice, granules are better for percolation methods while fine-mesh material is better for agitation and filtration. But the bleaching power of fullers earth is not spent by either of the single percolation and agitation methods and the retained oil is lost to the same amount almost as would be if the earth were spent by a series of agitations and percolations.

6. *Revivification of fullers earths.*

The most important thing to do in revivification of spent fullers earth is to get rid of the freed sodium which forms sodium hydroxide and saponifies the oil. It is not necessary to burn out all of the coloring matter if the alkali can be removed otherwise. Any temperature above 1200° Fahr. injures the bleaching power of fullers earth and when all of the combined water is driven off, the bleaching power is also damaged if not destroyed.

7. *Bleaching temperatures of fullers earth.*

Like enzymes, fullers earth seems to be somewhat but much less affected by extremes of temperatures. The earth should be free of free moisture as this makes the contact of the color compounds in the oil with freed H ions less. Then the oil must be of such a temperature that the H ions can get in contact with the color compounds and this varies for different grades of oils.

8. *Plasticity and hardness of fullers earth.*

As a rule the harder the fullers earth, the higher is its silica content and when this silica content yields a high relative acidity the better it bleaches and the less plastic will be the finely ground earth. So neither hardness nor plasticity directly affects the bleaching power of fullers earth. The bleaching power is inherent in the solid di-silicic acid. But in practice the hard granules are preferred when used in percolation.

9. *Activating clays.*

Fullers earth is a naturally-activated clay-like material. There are several clays or clay-like substances that can readily be activated by a proper acid treatment. Indianaite has hitherto been considered kaolin. When pure it contains about 40% silicon dioxide content, 40% aluminum oxide content and 15% combined water. Sulphuric acid will readily form alum out of the aluminum content and leave colloidal pectoid silica if the right amount and strength of acid is used at the right temperature and time. Too much and too strong acid will leave the silicon content as silicon dioxide which will not bleach. Hence this material is not an aluminum silicate nor a true kaolin at all. It is really di-silicic acid mixed with aluminum hydroxide. In activating it, it bleaches best when a small percentage (about 6%) of the original aluminum hydroxide is left in it. The presence of the aluminum hydroxide in some way permits the di-silicic acid to free more H ions than pure di-silicic acid. It takes a little less than its own weight of commercial sulphuric acid to activate it. Bentonite has only about one-half of the aluminum content that indianaite has and to activate it, about one-third of its weight of commercial sulphuric acid mixed in water is needed. Halloysite and a few other peculiar clay-like materials can be activated by simple acid treatment. But to activate sand or aluminum silicate clays, they must first be put in a colloidal state like indianaite, bentonite, etc. Hence bentonite is not necessarily of direct volcanic origin nor is indianaite of bacterial origin. They are colloidal alumina and silica made by the action of sulphuric acid, carbon dioxide, etc., mixed in underground water affecting certain clay deposits from which they are made just as fullers earth is made from inert or so called dead clay. Locally small patches of fullers earth are found that will bleach almost as much mineral oils as will the best activated clays.

The above proportions of acid and water are for activated clays used in treating neutral oils. More Al_2O_3 content of the clay must be removed for sulpho acid oils.

10. *Reasons why fullers earth contains di-silicic acid.*

(a). More or less plugging the pores of fullers earth or destroying them by fine grinding assists bleaching.

(b). All silica-containing bleaching compounds exhibit a relative acidity when they contain no soluble elements; and those with highest true relative acidity are best bleachers.

(c). All silica-containing bleachers precipitate as much pure ammonia sap brown as will an amount of weak acid which is equal to the bleaching compound's relative acidity, and free an equal amount of ammonia.

(d). All spent bleachers of acid-alkali treated oil contain as much soda as the bleachers relative acidity.

(e). Fullers earth spent bleaching sap brown will bleach again as soon as the freed alkali is removed so as to permit the earth to free more H ions. The same applies to vegetable and mineral oils.

(f). White heat will destroy the bleaching power of fullers earth and all silica-containing bleachers as will driving off all combined water because the silica turns into silicon dioxide.

(g). The aluminum hydroxide loosely associated with di-silicic acid in best bleaching activated clays or pure fullers earth acts like a co-enzyme. It takes no part in the reaction unless it furnishes the H and OH ions but its presence facilitates the greater production of H ions.

(h). Fullers earth does not adsorb basic ions. If the freed soda were continuously removed and if the precipitated color compounds did not bury the fullers earth so that the H ions could not get to the sodium color compounds, then fullers earth would bleach indefinitely, just as enzymes will act if the alleged or so-called catalyzed products are removed so as not to stop the action. Naturally the di-silicic acid must have traces of moisture to continue its work, as do enzymes.

(i). Bleachers burned to white heat cannot be revivified nor reactivated by a simple acid treatment. The silica and alumina must again be put into a colloidal state.

(j). Good bleaching fullers earth are only found under special conditions. They are primarily activated by sulphuric acid and colloidal silica. Activated clays are colloidal silica and alumina treated with acid in definite amounts, time, temperature, and manner or the bleaching material will be no good.

(k). No true aluminum silicate nor silicon dioxide will bleach nor cannot be made to bleach by an acid treatment until they are first put into a true colloidal state.

(l). There is no chemical reason why solid or pectoid di-silicic acid does not and cannot exist.

(m). Good bleaching fullers earths have 8 to 10% combined water which would be the amount of water for di-silicic acid when we make due allowance for the fact that fullers earth has only 60 to 70% silicon dioxide content and some of it is free silicon dioxide as fine sand and some is combined with aluminum.

Discussion

The facts that good bleaching fullers earth as well as activated clays have low aluminum, potassium and sodium oxide contents indicate that they are not clay silicates. The fact that both fullers earth and prepared clays are activated primarily by means of sulphuric acid indicate the same. The fact that all good bleaching silica-containing materials have a high combined water content and silicate clays have little or no combined water content prove that they are chemically different. The fact that silica can only be activated when in a colloidal state proves that the silica in prepared clays and fullers earth is in a different state than it is in ordinary clays.

Silica can act both as a base and as an acid. Sodium silicate and ortho-silicic acid are readily dissociated. Colloidal silicic acid is a positive or a negative colloid, according to the mode of preparation; and the two kinds are coagulated by addition of salts having negative and positive ions, respectively. There are known meta-sodium silicate, ortho-sodium silicate, meta-sodium di-silicate; but ortho-silicic acid is the only acid of silicon hitherto known. Even though ortho-silicic acid is the only known acid of silicon, the salts of silicon indicate that there are other silicic acids, representing different degrees of hydration of silicon dioxide. There should be meta-silicic acid, di-silicic acid, and tri-silicic acid.

If one treats commercial glass with too little sulphuric acid, it will not bleach much, if any. If you treat commercial glass with too much sulphuric acid, it will not bleach much, if any. If you treat commercial glass with a slight excess of sulphuric acid, wash and dry properly, it will bleach well and if you first add some colloidal aluminum hydroxide to the commercial glass and then treat it properly with sulphuric acid, it will bleach as well as the best prepared or activated clays. The temperature, the time, the concentration of the commercial glass and sulphuric acids must be correct to get the best bleaching compound. This bleaching material will have around 13% combined water which di-silicic acid also has, and commercial glass is a sodium salt of di-silicic acid. Hence when properly treated with sulphuric acid, hydrogen replaces the sodium of the commercial glass and the sodium then combines with the sulphate of the acid and one could have nothing more than di-silicic acid.

The same condition is noted when I added 20 cc. of commercial glass to 30 grams of XXF Floridin brand of fullers earth and using only enough water to make a thick paste and boiling gently for one hour and then adding 10 cc. commercial sulphuric acid and boiling for another hour gently; and then wash acid free and dry. This will bleach almost 50% better than the original fullers earth and retain much less oil. But if too little acid is added to the above mixture, it will not bleach as well as pure XXF. If too much or strong sulphuric acid is added, there is a violent chemical action accompanied by the liberation of hydrogen, sulphur dioxide, and carbon dioxide gas; the resulting material will not bleach as well as pure XXF. The same is true of the activation of bentonite, indianaite, halloysite or any other colloidal clay-like material in which di-silicic acid is mixed with aluminum hydroxide. All the conditions for the different materials must be proper if a good bleaching material is prepared.

The fact that fullers earth actually precipitates the color compounds, freeing soda and not adsorbing either the color compound or the soda gives us a new view-point of all similar types of alleged selective adsorption and catalytic action. In the case of fullers earth, the action is plain chemical action of a solid pectoid di-silicic acid freeing electrons which form special H ions. It behaves exactly like enzymes of the organic realm. Hence enzymes are doubtless colloidal organic acids which free specific H and OH ions under proper conditions to preform their function. There is also a parallel between activated carbon and activated silica. When carbon is once out of the pectoid state it cannot be activated. It also acts and bleaches color compounds exactly as does activated silica. Hence activated carbons that will bleach color compounds are doubtless solid carbon acid. And the alleged adsorption of hydrogen by platinum or pallidium may also be the formation of solid acids. Hence all catalytic action is probably nothing more than the action of colloidal or pectoid-like acids. If this is true of all cases, as it is of the action of fullers earth and activated silicon-containing materials, then the term adsorption in chemistry has no value as it is a misnomer. The process is electronic-ionic instead of atomic-molecular chemistry.

If my discovery of the mysterious power of fullers earth, which has hitherto been considered a catalytic action in some way associated with the pores in the earth and commonly termed selective adsorption, can be applied to all types of catalytic action, then in the near future one may look for the explanation of both muscular activity and nerve impulses, as they can be explained by the liberation of H and OH ions by colloidal material in the muscle and nerve fibers.

Some Additional Notes

The process of refining kerosene is generally thought to consist in the removal or decomposition of the aromatic hydro-carbons, fatty and other acids, phenols, tarry products, some sulphur compounds, etc., which lower the quality of the oil, sulphuric acid removing some, while caustic soda removes the remainder and neutralizes the acid which has been left in the oil. The petroleum loses in weight and the acid gains. The tar products dissolve and impart a deep brown color to the acid. While the aromatic hydrocarbons and many other unsaturated hydrocarbons are converted into sulpho-acids, and the acid is instrumental in removing the oxygen containing bodies. In fact, acid can be used until all oxygen is removed from the oil. But at first sulphur dioxide evolves in some quantity and is not explained or accounted by the above reactions. Of course with a proper acid or sulphur dioxide treatment sulpho acids are formed; but they bleach by some H and OH even if there is no soda to liberate.

Sap brown and vandyke brown have oxygen which can be removed by adding enough sulphuric acid to carbonize sap brown. Sulphur dioxide is liberated in quantity when poured on sap brown; red and yellow colors are produced and these colors are sulpho-acids. These colors appear brown in color when mixed together in a fairly concentrated solution.

The difference in results obtained by titrating mineral-oil acid sludge with alkali and those formed by determining the acid content of the same sludge gravimetrically as by barium sulphate is probably due to the fact that vandyke brown-like humic acids will combine with the alkali and do not with barium.

Ordinary Baku petroleum when exposed to the sunlight and air becomes strongly acid and gives off a penetrating odor, while there is deposited a yellow sediment. Acid red and yellow colors obtained from sap brown by strong sulphuric acid treatment also deposit a yellow sediment when exposed to sunlight.

Crude oil exposed to sunlight, with admission of air, in either clear or blue bottles, becomes darker in color and more acid in nature; whereas the same oil in orange and green bottles become lighter and no more acid. Air and sunlight will in time darken certain humic acids like vandyke brown. Light also causes oil to absorb air while darkness prevents oils from absorbing air readily. These facts have a bearing on how humic acids turn into vandyke brown when near the surface and into other forms when buried deeply in oil shales.

The absorption of nitrous oxide, carbon dioxide, and oxygen in oils is said to decrease in the dark but nitrogen and hydrogen absorption in oils increases in the dark. These above-reported facts may indicate how humic acids might increase their hydrogen content and lessen their oxygen content. in such a manner as to make crude oil. I have shown that asphaltum has been oxidized from azo-humic acid rather near the surface. Sulphuric acid produced from pyrite in oil shales or sands could also oxidize some of the azo-humic acids into asphaltum of crude oils.

The above facts may also indicate how green plants might utilize humic acids to produce oils found in them. In fact, most plant life needs more or less humus and all dense jungles have much humus. The humus not only holds moisture but also furnishes much extra carbon dioxide. The Amazon jungles have little limestone and yet they are luxuriant. Hence the Coal Measure swamps may also have obtained their extra carbon dioxide in a like manner and not by dissolution of limestone.

The great humic acid swamps color the dark brown waters which flow toward the sea and the salt water readily precipitates the coloring matter which are humic acids. These deposits of humic acid are perfectly enormous and continuous in certain regions of the earth. They become incorporated in the sedimentary series parallel to the old shore lines. Hence these original coloring matters from plants decaying in sandy swampy regions can and do appear again in the refining of mineral oil as well as vegetable oil. In fact, I believe that they are the chief if not the sole source of mineral oil. The azo-humic acids are either protein molecules from decaying plants or they are humic acids that incorporated their nitrogen content from sandy swamps. Azo-silico-humic acids may also be the chief source of the silicon content of plants and for this reason be so necessary for certain crops like corn, etc.

I found one patch of alum bluff formation fullers earth at Quincy, Florida in the midst of good bleaching fullers earth that would not bleach well. It contained a high lime content and a peculiar fossil fish oil. The latter may have prevented it from becoming naturally activated, as I could activate it.

I found that the Ordovician bentonite in Kentucky and Tennessee was thicker on the tops of anticlines and domes than on the flanks and adjacent regions. There are three thin veins near Frankfort, Ky. in a quarry and one mile down the river there is only one eight-inch bed, as there is near Tyrone and Gleen Creek. At Tyrone in the face of the bluff it is eight inches thick; and two hundred feet back, it is only two inches. There are also various thicknesses within a radius of five miles of High Bridge, Ky. but none of it is five feet thick. On the top of an anticline at Dayton, Tenn., it is three feet thick. Hence it does not materially thin towards the south. The analyses of the limestone just above and below indicate where the original calcareous clay got its extra colloidal silica from. Hence at least the Ordovician bentonite if not all bentonite, is not necessarily of direct volcanic origin. Its origin parallels that of unactivated fullers earth, indianaite, halloysite. etc. Bentonite of California is used to make filterol, etc.

Conclusions

1. Fullers earth and activated clays bleach oils by virtue of their disilicic acid precipitating the colors, by liberating electronic energy and some material like carbon, etc., filter out mechanically.

2. The chief colloidal coloring matters in oils are of an azo-humic acid nature, more or less affected by the acid-alkali treatment and heat treatment of oils. There are also humic acids like material.

3. Good bleaching fullers earth is activated in the region of the underground water level, primarily by sulphuric acid.

4. Porosity, plasticity, hardness, size of mesh, adsorption, etc., have nothing directly to do with the chemistry of fullers earth bleaching other than facilitating contact of H ions liberated by di-silicic acid with the color compounds.

5. Some, if not all, catalytic action is due to colloidal acids in a more or less solid state that liberate electronic energy as radium does.

6. Revivification of fullers earth is getting rid of alkali so di-silicic acid can free more ions.

7. Improvements in bleaching and losses of oils due to retention now seems possible.*

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* I wish to express my gratitude to the Floridin Company for the privilege of working in their laboratory at Quincy, Fla. This paper was prepared for The American Oil Chemists' Society meeting at New Orleans May 5-6, 1924, but withheld from publication (J. D. H.).

THE OILING OF LEATHER*

16-227

BY T. G. ROCHOW

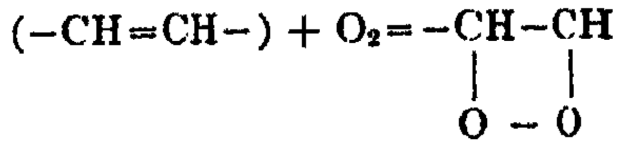
The use of oils on leather is one of the most important processes in leather manufacturing. Oil seems to be the cure-all of the tanner. Schlosstein[1] lists the following functions of oils and fats: leather-building, protecting, waterproofing, body-giving, weight-increasing, softening, lubricating, and preserving. Surely a theory explaining all these functions of an oil would be expected to be very complicated, and a review of the literature certainly does not disappoint the investigator on this point.

It has long been known that to give a satisfactory product the presence of water during oiling was necessary, except in the "burning-in" process whereby tanners found a method of stuffing heavy leathers by applying the hot grease or oil to the dry, hot leather. But in all the other processes for currying, water is one of the constituents. It was the explanation of the function of the water that was particularly bothersome to early investigators. Practical books on tanning still describe the "drawing-in" of the oil as the water evaporates.

Fortunately, in the past ten or twelve years considerable work concerning the oiling of leather has been published. It is the purpose of this paper to correlate these investigations and the theories concluded from them, demonstrating wherein they conflict or coincide with the findings in our experimental work or that of other investigators.

Chemical Combination Theory

Quite recently considerable work has been done to explain the oil tannage of leather. Most of the theories seem to agree with that of Fahrion[2] which is substantiated by L. Meunier[3]. Briefly, this theory involves the oxidation of the unsaturated bonds in fish oils:



$$(-CH=CH-) + O_2 = \begin{array}{c}-CH-CH\\ \quad | \quad\;\; | \\ \quad O - O\end{array}$$

These bi-peroxides (the oils contain two or more double bonds) act upon the proteins, one peroxide attacking the amino groups which are oxidized by loss of hydrogen: the hydrogen thus liberated transforms the oxygen of the second peroxide group into two hydroxy groups; finally one of the hydroxy-groups thus formed lactonizes the carboxyl of the fatty acid. Another portion of the peroxide acids undergoes molecular rearrangement, causing the appearance of hydroxy groups which form lactones with the carboxyl

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* This work was done as part of the senior thesis under Professor Bancroft.

[1] J. Am. Leather Ass., 14, 41 (1919).

[2] Z. angew. Chem., 1903, 665, 1911, 361.

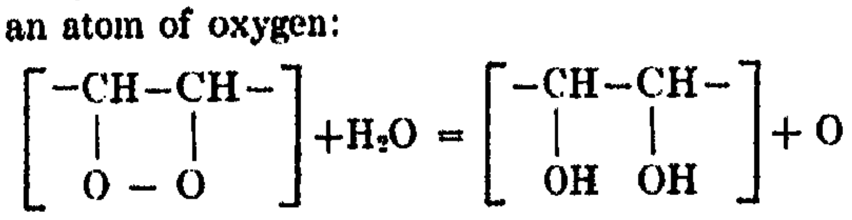
[3] J. Am. Leather Chem. Ass., 13, 530 (1918).

groups. These lactones are retained by the fibers, preferably because they are insensitive to alkaline washing.

It was only natural that this theory be applied to the oiling of leather in general because marine oils for a long time have been the most used by tanners. Schlosstein[1] in an article advocating the use of fish oils for currying leather, states that "to a certain extent the "active principle" of fish oils is always formed when oil is applied to leather and that, therefore, currying cannot be considered as a purely physical lubricating and softening but as a combined physical and chemical process in the nature of a second tannage."

Moeller[2] uses the oxidation theory more completely as a theory explaining the waterproofing and other properties given leather by fish oils as well as a method of explaining the old question of the functions of water during the process.

Water hydrolyzes the peroxides formed on oxidation of unsaturated fish oils yielding an atom of oxygen:



$$\begin{bmatrix} -\mathrm{CH}-\mathrm{CH}- \\ | \qquad | \\ \mathrm{O} - \mathrm{O} \end{bmatrix} + H_2O = \begin{bmatrix} -\mathrm{CH}-\mathrm{CH}- \\ | \qquad | \\ \mathrm{OH} \quad \mathrm{OH} \end{bmatrix} + \mathrm{O}$$

This oxygen oxidizes the polyphenols of the free tannins in the leather to give quinone compounds similar to the phlabophenes. These products are good tanning agents just as the phlabophenes are. They increase the water resistance of the leather since they are in themselves insoluble.

As long as there is hide substance to be tanned, fish oils are going to tan it whether they are introduced primarily to tan the leather or to oil it. But as a general theory explaining the functions of an oil in leather currying, this theory is very limited in its applications, since it applies only to vegetable- and oil-tanned leather and not to chrome- or alum-tanned leather. It cannot apply to animal oils and vegetable oils containing little oxidizable substance or to mineral oils. These classes are largely used in practice and work very well. Schlosstein himself, in the article referred to, says that hydrogenized oils are coming into use. As for the fish oils themselves, when used on vegetable-tanned leather, it is difficult to see how these oxidized tannins are very active in the softening, lubricating, or any other of the functions of a leather oil as listed by Schlosstein, except, as Moeller states, that of waterproofing. As a method of explaining the use of water in the process the theory is equally weak. Moeller says that "evaporation of the water is very improbable on account of the isolating fatty layer." The vapor pressure of two immiscible liquids is equal to the sum of the vapor pressures of both, so that this assumption is not valid, though the rate of evaporation will be decreased if the oil layer is outside. Moeller then goes on to state that the water is not necessary as a means of "drawing" the oil into the leather but merely acts as a reacting substance converting the $C=C$ group into oxyacids. As proof he uses the well-known fact that dry leather will adsorb train or any other oil

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[1] J. Am. Leather Chem. Ass., **14**, 41 (1919).

[2] Der Gerber, **45**, 277 (1919).

but very slowly and leaves the surface slowly. As a matter of fact, even if every oil used on leather were a drying oil, and if every drying oil classed as such, were composed entirely of unsaturated compounds, the amount of water used on the leather is many times that necessary to hydrolyze the peroxides when one considers that most leathers contain only 5-15% of their weight of oil and that the molecular weight of the oil so high that the combining weight of water would be extremely small. Besides air-dried leather contains about 5 or 6% of moisture, more than enough to hydrolyze the peroxide of the oils.

Moeller says that the oxidation of the oil is strongly influenced by the phenolic compounds of tanning agents as confirmed by the presence of oxy-acids in the dried train oil. Why one would not attribute this to ordinary oxidation is not known.

In a later article Moeller[1] tried to determine whether train oil was most greatly changed by tannin, leather, hide, or simply by the air. His theory was *not* well substantiated by his results, since pure tannin was next to the lowest in making train oil insoluble and the least effective in reducing the iodine number of the train oil.

The chemical combination theory has also been dragged into use to explain why solvents will not extract as much oil, after some time, as they did soon after the oil was applied to the leather. Lauffmann[2] states that all ordinary fat solvents (ethyl ether, petroleum ether, carbon tetrachloride) except chloroform and carbon disulfide extracted less oil after 120 days than after 2 days standing. He says that the low results were probably caused by combination of fat with the hide substance. Turkey Red Oil (sulfonated castor) gave the same results as did degras, so the oxidation products of the oil cannot be the combining substances. In the article referred to, Moeller[3] says that oil not removed by solvents is not necessarily combined with the collagen because it is difficult and sometimes impossible to remove oil even from emulsions. He goes on to state that the retention of fatty acid and glycerides in leather is intelligible on the basis of colloid-chemical theories of emulsions. It was to disprove the oil-collagen combination theory that he attempted to show that train oil reacted with tannin and therefore was insoluble in petroleum ether.

When he found that train oil was only 25% soluble in petroleum ether when mixed with equal amounts of various tanning extracts and kept three days, he immediately assumed that chemical combination had taken place, after stating that oils were difficult to remove from any emulsion. His attempts to prove combination between the oil and tannin seemed to have failed. He mixed 100 grams of each of various tanning agents with 40 grams of train oil and compared results with a 45% solution of pure tannin mixed with 40 grams of train oil. The tannin was next to the least active in making the oil insoluble. It was next to the best in increasing the acid value, but it

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[1] Z. Leder und Gerberei Chem., 1, 20 (1921).

[2] Ledertechn. Rundschau, 19, 63, 71 (1927).

[3] Der Gerber, 45, 277 (1919).

was least effective in saturating the desirable bonds as shown by the highest iodine number and lowest values for oxy-fatty acids.

There is a great difference of opinion as to the desirability of the use of mineral oils on leather. A brief discussion is brought in here to disprove the theory that an unsaturated oil is necessary for the proper currying of leather.

Grasser[1] says that mineral oils are widely used for leather and that vaseline oils are the most important. The paraffine and ceresines are also excellent preservatives. He recommends sulfonated castor oil merely as an emulsifying agent.[2] Hart[3] states that mineral oils are widely used by the leather industry. Buncke[4] gives a blow to the oxidation theory when he states that spotting is caused by an excess of oxidized fatty acids or lack of sufficient alkali to neutralize the acids liberated by sulfonated oils. He recommends sulfonated oils merely as emulsifiers for neutral oils. This is in accordance with Mezey's[5] work in which it was found that the greater the proportion of unsulfonated neatsfoot oil, or mineral oil, in mixtures of these with sulfonated neatsfoot oil or train oil, the greater the adsorption of the oil by chrome leather, unless the sulfonated oil was in too little quantity to emulsify the unsulfonated neatsfoot or the mineral oil. Schindler[6] also says that free fatty acids and oxy-fatty acids should be as low as possible and that sulfonated oils act only as emulsifying agents. Whitmore, Hart, and Bach[7] showed that petroleum plus paraffin gave nearly as great an increase in tensile strength, with strap and harness leather as did a mixture of tallow, cod oil, and wool grease. They state that the increased tensile strength is due to lubrication and strengthening of the leather fibers. Very few investigators deny that mineral oil can be used with satisfactory results to oil leather. Kinsky[8] seems to think that wool fat, mineral oil, or resin, hinders the penetration of a degras fat liquor and causes spotty or cracky leather. But he is in the minority and in general we may say that mineral oil is a satisfactory leather lubricant if applied correctly. Only its physical properties need be changed and it will work as well as the animal and vegetable oils. Therefore, any chemical combination theory would have to explain the satisfactory oiling by the inactive, neutral, mineral oils.

Co-precipitation of Colloids Theory

J. A. Wilson[9] explains the process of fat-liquoring by the co-precipitation of colloids. He takes chrome leather stuffed with an oil emulsified by soap in water as an example. Wet chrome leather in acid solution assumes the following charge:

$$(NH_2-HC_1RCOO)_3Cr = (NH_3RCOO)_3Cr^{+++} + 3\ Cl^-$$

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[1] Le Cuir, 12, 121 (1923).

[2] Grasser: Z. Leder und Gerberei Chem., 2, 112 (1922).

[3] Ind. Eng. Chem., 21, 85 (1929).

[4] J. Am. Leather Chem. Ass., 22, 621 (1927).

[5] Collegium, 1928, 209.

[6] Collegium, 1928, 241.

[7] J. Am. Leather Chem. Ass., 14, 128 (1919).

[8] Schweiz-Leder-Ind Z., 1925, No. 24.

[9] J. Am. Leather Chem. Ass., 12, 120 (1917); 14, 458 (1919).

The globules of oil in the emulsion having adsorbed stearate ions are charged negatively. The oil globules are thus electrically attracted by the positively charged leather and precipitated on the leather.

Shorter[1] shows that in vegetable tanning, the leather assumes the charge of the negative colloid, tannin. He proved it by rubbing leather and wood together, the leather assuming a positive charge. Unless, the, vegetable-tanned leather adsorbs positive ions strongly from solution, Wilson's theory does not seem to work for vegetable-tanned leather.

According to Wilson[2] the penetration of the oil is dependent upon the size of the oil globules in the emulsion. Coarse unstable emulsions precipitate out on the surface of the leather giving it a dirty smeary appearance, and fine stable emulsions penetrate deeply before they are broken, giving a clear-grained, but loose, raggy, leather. pH also affects penetration. Wilson says that it is necessary then to lubricate only the outer fibers to give strength, softness and pliability, and to leave tne middle layer unlubricated in order to give tightness and "temper" to the leather with sulfonated oils. These views are upheld by Stiasny[3] who reports that an emulsion for fat-liquoring should be stable enough to penetrate the leather but not too stable because the oil must be deposited in the leather. Orthmann[4] agrees with Wilson when he reports, in an article of practical information, that too much sulfonated oil causes looseness of the leather fibers.

In his Chandler Lecture Wilson[5] makes a distinction between the mechanism of fat-liquoring chrome leather with sulfonated oil, egg yolk and water, and fat-liquoring or hard-stuffing with neutral oils and water. He says that sulfonated oils do not diffuse towards the middle of the leather during drying but remain fixed by a chemical combination between the sulfo-fatty acid groups of the oil with the chromium atoms. This theory, of course, does not apply to vegetable-tanned leather and if the co-precipitation of colloids theory is to be applied to vegetable-tanned leather some one will have to prove whether the leather adsorbs cations to overcome the negative charge given the leather by the tannin.

Wilson makes still another exception when he mentions that neutral oils do not penetrate the leather during fat-liquoring but merely become lodged in the outer layers, until drying takes place, when the oil replaces the water lost by evaporation. In this way Wilson tries to explain the application of neutral oil to wet leather in the hand-stuffing process. Wilson's assistant, H. B. Merrill[6], shows that for sulfonated neatsfoot oil and water emulsions using borax or sodium carbonate as emulsifying agents, most of the oil is present near the grain and flesh sides, and very little is present in the middle. More is present near the grain than near the flesh, and the oil does not change

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[1] J. Soc. Dyers and Colourists, **36**, 299 (1920).

[2] J. Am. Leather Chem. Ass., **22**, 559 (1927).

[3] Collegium, **1928**, 230.

[4] J. Am. Leather Chem. Ass., **23**, 351 (1928).

[5] Ind. Eng. Chem., **21**, 188 (1929).

[6] Ind. Eng. Chem., **20**, 181 (1928).

its position after drying or any subsequent time. With constant volume of fat liquor, the quantity of oil adsorbed is in direct proportion to the concentration of the oil and the fraction of oil taken up from the liquor is thus always constant, (approximately two-thirds in Merrill's experiments.) Increase in oil concentration in the emulsion does not increase penetration unless the ratio of oil to leather becomes very large. Using a fixed ratio of oil to leather the amount of oil adsorbed by the leather decreases as the volume of the fat-liquor increases but the penetration is little effected. The quantity of oil taken up increases with the time up to four hours and *thereafter* remains *constant*. By increasing the time from one-half to four hours, increase in oil content took place only on the outer layers.

Shifting the pH of either the oil or the leather had little effect on the total quantity of the oil taken up, but an increase in pH produced an increase in the penetration of the oil. It is probably on these results that Wilson based his chemical combination theory. It is unfortunate that Merrill did not run parallel experiments on an unsulfonated oil. The co-precipitation theory was weakened when it was found that the pH value did not affect the quantity of oil adsorbed; but greater penetration by a more stable emulsion made by raising the pH was substantiated.

In later experiments, using the same oil (sulfonated neatsfoot), but using egg as an emulsifying agent, Merrill[1] showed that distribution of the oil was the reverse of that using sodium bicarbonate or borax as emulsifiers. The white, yolk, or whole egg, each caused a higher concentration of the oil in the flesh side and, for the egg yolk at least, as tne egg content of the fat liquor is increased, the ratio of oil content of the grain, to that of the grain, decreases. Merrill explains this by assuming that egg yolk makes an emulsion of sulphonated oil less stable, which means coarser globules. These coarser globules cannot penetrate the close-textured grain and, in limited time and limited quantity of oil, more oil will be taken up by the flesh than by the grain. But with a fine-textured emulsion as that of sulfonated oil alone, the oil penetrates from both sides of the leather. Since directly under the grain surface there are less fibers per given volume, and because of the voids left by destroyed glands, there is less percentage of oil by weight in the grain than in the flesh.

Of course this theory is based on the assumption that egg decreased the stability (or particle size) of the neatsfoot oil emulsion. Merrill's description of the kind and part of the egg used are very confusing since in his procedure he states that commercial whole egg was used, yet the corresponding graphs and table refer to the effect of egg yolk. With this discrepancy it is difficult to determine from Wilson's own experiments[2] whether the emulsion is decreased or increased in stability, for yolk alone increased only very slightly the stability of 10 grams of equal parts of sulphonated and neutral neatsfoot oil in 100 grams of emulsion while thickened whole egg made an extremely stable emulsion. But, since all parts of the egg were shown to Merrill to

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[1] Ind. Eng. Chem., 20, 654 (1928).

[2] J. Am. Leather Chem. Ass., 22, 559 (1927).

concentrate the oil in the flesh side of the leather, it seems that the whole egg would have to make an unstable emulsion also in order that Merrill's theory be correct. Wilson proved otherwise. The only joker is that Wilson used equal parts of neutral and sulfonated neatsfoot oil while Merrill used all sulfonated neatsfoot. This difference seems slight because half sulfonated oil ought to be sufficient to make an egg-oil-water emulsion unstable if it is able to do so. More work should be done on this.

The work of Balderston is important because he found that greases and oils applied to dry leather on the flesh side penetrate and even concentrate in the grain side of the leather. Thus water is not necessary to disperse the oil, nor to "draw" the oil in by evaporation of the water, nor for any other mysterious reason. Balderston[1] performed a number of experiments in which he applied hot grease to leather allowed to stand for various lengths of time (4 to 14 hours) and then split them into three equally thick sections. By a series of hot extractions he found that in all cases the grease penetrated from the flesh through to the grain side and that, if the leather was heated after greasing, the grain contained much more grease than the flesh side. Using an emulsion of the grease in water, approximately equal amounts of grease were deposited in both outside layers. In all cases the middle layer contained less than half the amount of grease held by the flesh layer.

In a later article Balderston[2] showed that cod oil and linseed oil displayed the same phenomenon of penetrating through the leather from the flesh side and showing a higher concentration in the grain side after distribution. Balderston also showed that while heating did cause less fat to be extracted by petroleum ether the difference was very slight and seems to be not very much beyond experimental error in fat extractions. Linseed oil showed only a drop of 21.58 to 21.09, cod 29.15 to 27.87, and neatsfoot 33.65 to 32.76. The chemical compound theories are jolted heavily by Balderston's results, though Balderston seems to think that the above data are sufficient to prove a fixing of the oil in leather.

Interfacial Tension Theory

There is still another theory for the use of water in oiling leather. This is based on the fact that the interfacial tension between some oils and water is less than the surface tension of these oils in air. This theory was advanced as early as 1911 by Bennett.[3] He based his assumption on practical processes, and unfortunately not much has been done on the interfacial tension between various oils and water until very recently.

Bennett claims that water penetrates leather more easily than oils because its surface tension is much lower, so that it is able to present a greater surface to the leather fibers. Not only that, but the interfacial tension between many oils and water is much less than that of oils and air. In hand-stuffing, then, where the leather is first wetted and then oiled, the oil presents

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[1] J. Am. Leather Chem. Ass., 17, 405 (1922).

[2] J. Am. Leather Chem. Ass., 18, 475 (1923).

[3] Leather Trades Review, 44, 186 (1911).

a much greater surface to the leather fibers if it is in contact with a water surface. In emulsions, the emulsifier lowers the interfacial tension even more. In the "burning in" process successful currying is accomplished because the surface tension of the oil or grease is lowered by heating the grease and keeping it warm on the leather until penetration takes place. In "drum-stuffing" the leather is oiled wet and while hot. The combination lowers the surface tension still more. In fat-liquoring the interfacial tension is lowered between the oil and water by emulsifying agents such as egg-yolk, degras, borax, etc. The fat liquor is usually warm so that we have the three factors of heat, water, and a dissolved substance all reducing the interfacial tension of the oil. Bennett recognized the fact that while tanning isolates the fibers to some extent, yet a lubricating agent is necessary to separate the fibers still more and lubricate them so that they might slip easily over one another. He also realized that the nature of the oil and the method of application were not the only factors influencing penetration, but that the nature of the leather and its treatment during tanning also effect the degree of lubrication by regulating the degree of isolation of the fibers.

Certainly, the whole question of fat-liquor emulsions is one of surface tension and Bennett's explanations of the other methods of leather oiling are substantiated by recent measurements of interfacial tension between various oils and water.

Du Noüy[1] gives the following interfacial tensions between pure water and the following oils at 23°C.

Oil	S.T. Air Interface	S.T. H^2O Interface
Castor Oil	36.4 Dynes/Cm.	15.4 Dynes/Cm.
Olive Oil	33.0 "	11.0 "
Paraffin Oil	32.0 "	47.0 "
Liquid Petrolatum	33.0 "	49.0 "
Oleic Acid	34.2 "	12.8 "
(Water	72.8 " at 20°C. Chem. Rubber Pub. Co.)	

The mineral oils seem to have their tensions raised by water while those of oleic, castor, and olive show a lowering of interface tension. The mineral oils both showed a rise in the surface tension to water from that to air. This explains why in the use of mineral emulsifying agents of various and sometimes complicated natures are added even in the band stuffing process.

Schindler[2] found that all the commercial emulsifiers such as soap, sulfonated oils, sodium hydroxide, and sodium bicarbonate decreased the interfacial tension between water and fish, neatsfoot, olive, and vaseline oils. He found that egg yolk produced practically no effect on the interfacial tension of fish oil and water. But it was not raised, so Merrill has yet to prove that egg yolk increases the particle size in sulfonated oil-water emulsions.

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[1] "Surface Equilibrium of Colloids," 166.

[2] Collegium, 1927, 288.

Theoretical and Experimental

The more important investigations of the mechanism of oiling leather have been described briefly. All sorts of complicated theories of chemical combination of neutralization of electrical charges, have been advanced. These all are very narrow in their application to the process as a whole, and in most cases are highly, and admittedly speculative. The oxidation theory of Fahrion, Meunier, and Moeller is applicable only to vegetable-tanned leather oiled by oils containing a large percentage of unsaturated fatty acids. Even then, the theory gives no explanation for the use of water many times that necessary for the hydrolysis of the peroxides formed in the oils by oxidation. Wilson's co-precipitation theory applies only to chrome leather and fat liquors. And his chemical compound theory applies only to chrome leather and sulphonated oils.

The simplest theory is very often the most applicable. The following explanation falls into this category. After tanning, the collagen fibers are separated somewhat by destruction of elastin, fat, and the portions of the epidermal system distributed in the corium minor. But still the leather is hard and stiff so that further lubrication of the fibers is necessary. To lubricate the swollen fibers and fibrils they must first be separated. This is the real function of the water. (1.) The oil can then be adsorbed by even the tiniest fibers because it wets them in preference to water, as will be proved later. (2.) All the other processes are necessary to reduce the surface tension of the oil in order that it may present a greater surface. (3.) Each of these functions will be discussed in turn.

(1.) *Swelling the Fibers.*

Bennett[1] recognized the importance of isolating the fibers of collagen in preparing a soft, flexible leather, when he listed the nature of the tannage as a factor in determining degree of penetration of oils. His reason was that the degree and nature of the tannage determines the degree of isolation of the fibers. The only trouble was that he explained the function of water in oil by stating that water penetrated leather more easily than oils because its surface tension was less. Reference to du Noüy's table shows that at room temperature the surface tension of water is twice that of most oils used on leather. The real reason is that water can swell the fibers and separate them; and oil cannot. Therefore, we add water to swell the fibers and then oil to keep them separated. If the fibers are once separated it makes little qualitative difference how the oil is applied, whether by hand swabbing, drum stuffing of the wetted leather, or by an emulsion of oil in water. Indeed one patent[1] has been taken out to cover a process whereby the wet chrome-tanned leather is steeped in acetone until the water content is reduced to 14 to 20%. The acetone is removed and the leather treated with stuffing material. The next step from this process would be to remove all the water without allowing the fibers to glue or stick together again. The following experiments prove

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[1] Leather Trades Review, 44, 186 (1911).

[1] Pickard, Lloyd and Caunce: U. S. Pat. 163877 (1928).

that this may be done by using gradient alcohol solutions and that a very *soft flexible leather results.*

Oak-tanned cow hide (containing 0.861% natural oil by petroleum ether) was cut into strips one inch wide and three inches long. Four pieces were used. They were all soaked in distilled water one day. Sample No. 1 was dried. Sample No. 2 was immersed in cod liver oil (Squibb's Medicinal) one day, removed and dried. Sample No. 3 and 4 were transferred from the distilled water to a 50% ethyl alcohol and water solution. They were allowed to remain in this solution one day and about one day in each of the following solutions, in the order given and without intermediate drying; 67%, 82%, 95%, and absolute alcohol, and xylene. Sample No. 3 was removed and dried to be used as a "blank." Sample No. 4 was immersed in a 15% solution, by volume, of the cod liver oil in xylene. It was removed after one day and dried for two days in the air.

After all samples had dried at least two days they were compared. Sample No. 2 of course was softer than No. 1. Sample No. 3 was softer than both; so prolonged immersion in the solutions did have a softening effect, due to the extraction of water solubles and substances used to increase the weight of the cow hide. But Sample No. 4 was very much softer than No. 3. It was the most pliable of any cow hide oiled in these experiments.

Conclusion: A very soft and pliable leather is obtained by displacing the water completely from thoroughly-wetted cow hide leather by alcohol solutions and introducing cod oil by means of a solution in xylene. Part of the flexibility was due to extraction of solids by the solutions but the oil made a very flexible leather when introduced in this way.

Using the same procedure, mineral oil and castor oil also gave a very flexible leather though not quite so soft as the one oiled with cod liver oil.

In tanned leather, the fibers are isolated somewhat from each other by the tannin. In raw hide, the fibers have no such isolating material and consequently the fibers cohere as soon as they become dry, and a hard, bony mass results. In pure water the fibers swell and become separated. If we could get a lubricant between the fibers while the hide is in this condition, the skin would remain soft and pliable. This was successfully accomplished experimentally. Pickled sheepskins as received by the tanner, ready for tanning, were used. They were pickled in sulphuric acid and salt. Since they were beamed, bated, and limed, removing the fat, epidermis, and elastin, we may consider the sheepskins, ready for tanning, as nearly pure collagen. The pickled sheepskins were cut into pieces about two inches square. They were soaked in distilled water for 24 hours. The water was changed and the skins allowed to soak for 24 hours more. Then the gradient solutions of the histologist were again brought into play. The skins were soaked 24 hours or more in each of the following, and in the order given; 50% alcohol, 80%, 95%, absolute alcohol, and xylene. One piece was removed and dried to be used as a blank. The others were cut in two and marked in pairs. One of each pair was immersed for two days in xylene solutions, 10% by volume, of the following oils; codliver oil (Squibb), white medicinal mineral oil, and pure castor oil. The other pieces were dried three days and each immersed in the oil corresponding to that used for the other sample of each pair.

It is well-known that alcohol gives a pseudo-tanning to animal skins, but that the treated skin swells in water and is converted to gelatine on boiling just as the untreated raw skin is. For some reason not understood, the fibers do not stick or glue together on drying but remain partially separated. Thus, the blank made in this set of experiments looked more or less like leather, but it was stiff, hard, and somewhat shrunken. On boiling with water it was converted quickly to gelatine.

The samples dehydrated and oiled by solution without intermediate drying were all remarkably soft and flexible. The sample immersed in mineral oil was less flexible and had shrunk more on drying. It was, however, considerably softer than the blank. The other samples of the pairs, which had been dried before being placed in the oil solution were no softer than the blank and of course had shrunken just as much since they received no more swelling by water after drying. The one dried and then oiled by cod oil was slightly more flexible than the blank but far stiffer than the sample oiled by cod oil without previous drying.

Both samples oiled with mineral oil went into colloidal solution on boiling, the oil going partly into emulsion and the rest floating on the water. Most of the skins oiled by castor oil formed a sol on boiling, although a few quite small gelatinous pieces about a millimeter in diamater resisted the action of boiling water. Both samples of the pair, however, reacted the same way towards boiling, so the difference in flexibility between the one oiled while swollen, and the one oiled after drying was not due to the fact that the first was tanned and the other was not. Little of the cod-oiled skins went into colloidal solution on boiling. Appreciable tanning by the cod liver oil was apparent, but here again both reacted the same way toward boiling water. The raw skins dehydrated by gradient alcohol solutions and oiled by xylene solutions were more flexible and softer, than the ones that were dried previous to oiling, because the fibers of the first samples were kept continually swollen and separated during oiling while those of the second series of samples were allowed to stick together before oiling.

Pieces of the pickled skin washed, and swollen in distilled water, dipped in oil (one in cod liver, the other in castor oil) became hard and brittle as soon as the water had evaporated. Another sample was dehydrated by the gradient alcohol solutions, soaked in xylene, dried five days, and then immersed in the castor oil-xylene solution for a day. It was as stiff and hard as the blank, as shown before. It was hoped that, by soaking it in water, the fibers would swell and become separated without displacing the water. But water is as easily adsorbed by collagen as by gelatin and the adsorbed oil was therefore displaced by the water and was seen floating on top of the water. Consequently, the skin dried in to a horny mass as though untreated. It is, therefore, necessary to remove the water before oiling untanned skin, but the fibers of collagen must not be allowed to cohere.

It is interesting to note that the above reactions are entirely reversible. A sample treated similarly to the one just described above likewise became a horny mass when dried, after soaking in distilled water for 2 or 3 hours, again running the sample through the gradient solutions and the castor oil-xylene solution, this time without intermediate drying, rather a soft flexible product was again obtained. The reactions thus are truly reversible.

Conclusions: Untanned skin swollen by pure water and kept swollen through the gradient solutions, which removed all the water, when immersed in a xylene solution of the oil remains soft and flexible on drying; while skin treated the same way but allowed to dry before immersion in the oil solution remains as hard and stiff as an unoiled, but otherwise similarly treated, piece of skin. It may be concluded then that the function of water in the oiling processes is to swell and separate the fibers so that the oil may penetrate between the smallest fibers and fibrils, lubricating them and keeping them from cohering.

(2.) *Preferential Wetting of Leather by Oil:*

The question naturally arises as to how oil can displace water from leather fibers, since tanned leather exhibits the ability to adsorb water and swell just as untanned collagen does, but to a much less extent than collagen. Water was seen to displace castor oil from untanned skin, making things look dark for advocators of a theory of preferential wetting of leather by oil. But the theory of preferential wetting of a solid emulsifying agent by the external phase of an emulsion, helped us out of our difficulty. If a solid emulsifies water in oil, it has been shown[1] that the solid is wetted partially by both liquids but preferentially by the oil, since the solid lies on this side of the interface.

The oak-tanned cow hide previously described was ground up and extracted eight hours by petroleum ether in a Soxhlet extractor. Twenty c.c. of the medicinal cod liver oil was added to 25 c.c. of distilled water in each of three glass stoppered bottles. To one no emulsifying agent was added. In the second bottle the ground leather was soaked in the oil a few minutes and then the water added. In the third bottle the leather dust was soaked in water first and the oil added. Each bottle heretofore not agitated, was shaken one minute. The first emulsion settled in 1 second, the second in 23 seconds, and the third in 5 seconds. On repeated intermittent shaking the second emulsion became very stable, lasting for hours, while the third emulsion continued to settle in 5 or 10 seconds during the first day. The mixture of oil and water continued to settle out in 1 or 2 seconds throughout these experiments. The mixtures were allowed to stand the next day without agitation. During all the third day the emulsions showed little change in the relative stability although mixtures Nos. 2 and 3 seemed both a little more stable than on the first day. The two emulsions were proudly displayed as a peculiar example where in the adsorbed water on the leather dust in the third sample was not displaced by the oil which is sample No. 2 made a stable

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[1] Bancroft: "Applied Colloid Chemistry," 352 (1926).

emulsion by wetting the leather. By noon, however, sample No. 3 refused to work as it was scheduled, but remained an emulsion as long as No. 2. Repeated shaking during the morning had wetted the leather with oil.

These experiments were repeated using a finer leather dust (about 75 to 100 mesh). This time the oil displaced the water on the leather dust much quicker (in an hour of intermittent shaking). In this run and in the previous one, the emulsion was definitely proved to be water in oil by adding a drop of oil to a small portion of the emulsion. The drop of oil disappeared immediately, while a drop of water when added to the emulsion remained in a separate globule.

Similar emulsions were not obtained for castor oil or mineral oil using the same proportions. The usual precautions in preparing emulsions were not followed, however. The leather dust was simply wetted by the desired phase and the oil and water poured together and shaken. More work should be done on this to determine whether by slow additions of the water with intermittent shaking or whether changing the proportions will not produce an emulsion in the presence of leather dust.

Conclusions: Cod oil, at least, wets leather in preference to water but the displacement of water by oil is quite slow, proving that leather is wetted almost as easily by water. This is why an under-oiled piece of leather may be saturated with water, when immersed in water.

(3.) *The Interfacial Tension between Water and Oil:*

It is apparent that, to get greater penetration of an oil into leather, the oil must present a greater surface to the leather fibers while they are swollen and separated. Since water is necessary in oiling, to swell the fibers, the interfacial tension between water and oil is very important. From du Noüy's table we find that with castor, olive, and oleic acid the surface tension in air is 2.4, or more, times as great as the surface tension in water. This explains why these oils work so well by simply swabbing them on wet leather. The mineral oils, however, show a surface tension in air 1.47 to 1.48 times less than that in water. This explains why we obtained such a stiff leather when wet cow hide was oiled with white medicinal oil. In practice mineral oil is always mixed with soap, sulphonated oils, or an animal oil to reduce its surface tension in water.

Microscopical examination verifies this. Droplets of cod, neatsfoot, castor, and olive oil all increased their surfaces when droplets of water were introduced to them, while a mineral oil droplet showed a decided decrease in size when water was introduced to it.

Small (one square centimeter) pieces, of the cow hide described, were dehydrated by gradient solutions of water and alcohol. The alcohol was displaced by xylene, and the xylene displaced by xylene-paraffin solution. The time in each solution was at least one day. The samples were then immersed in molten paraffin and then imbedded in paraffin. Sections were cut on a microtone, the paraffin dissolved out by xylene, the xylene by alcohol, and the sections were dried. The oils to be used were dyed with Sudan 3 to make them visible in water. Results in later experiments (using oblique illumination) were the same so the dye did not change the surface tension of the oils enough to affect the results.

The dried sections were wetted at their edges by the oils mentioned in the preliminary droplet experiments. But penetration was very slow, it taking hours for the oils to penetrate visibly even the very thin sections used. [This does not exclude that some oil was adsorbed within the sections.] All the vegetable and animal oils used, when introduced at the edge of the *wetted* section of the leather spread out to conform with the surface of the water. When this surface retreated across the section the oil followed it. As soon as the oil came in contact with the fibers they soon became transparent showing they had adsorbed the oil.

With mineral oil the appearance of the film in the presence of water was quite different. Instead of spreading out the oil droplet contracted in the presence of water, and as the surface of the water changed the oil droplet remained fixed in position. After all the water had evaporated the oil droplet was still stranded from the surface of the leather section. It had to be mechanically pushed to the surface of the leather and then its penetration into the fibers was so slow that it could not be seen after an hour of patient waiting. After a day or so it had penetrated into the section as did the droplet of mineral oil introduced on a dry section. Thus, while water separates the fibers, this advantage is lost because the interfacial tension between water and oil is too great to allow penetration while the fibers are isolated in water.

It is very interesting to note that Shereshefsky[1] found that two immiscible liquids in a capillary tubing will move in the direction of the one having the greater surface tension. This will explain the action of the animal and vegetable oils in the microscopic sections.

Attempts to duplicate the microscopic results in larger pieces of leather have failed. Pieces of the cow hide weighing 30 grams were soaked in water one hour and one end dipped in oil. When the exposed end was dry, the pieces were removed and cut in three sections parallel to the end dipped in oil. The sections were then ground up and extracted with petroleum ether. No difference in oil content between the middle and top sections was found. The trouble was that the sections were rectangular and the short side exposed to the oil. Thus the oil had to rise too high to be detected in the middle section. Experiments should be repeated dipping the long end in the oil.

The decrease in surface tension of an oil on heating explains why the "burning in" process is successful in currying heavy non-flexible leathers. In this process the hot oil is applied to the hot dry leather. It has been shown[2] that the grease or oil penetrates very well in this method. Water is not used and therefore as soft and pliable a leather is not obtained as though

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[1] Nature, **122**, 312 (1928).

[2] Balderston: J. Am. Leather Chem. Ass., **17**, 405 (1922).

the fibers had been separated. But "burning in" is used to give strength and water proofness to heavy leathers like belting and harness leather, where softness is not so desirable.

Conclusions: To give greater penetration more surface of the oil must be offered to the leather fibers. For most vegetable and animal oils the water alone, which is already present to swell the fibers, is sufficient to reduce the surface tension of the oil. These oils are therefore used alone with water in hand or drum stuffing. If mineral oil is used, substances must be added to reduce its surface tension. In fat-liquoring the surface tension of the oil is already reduced to form the emulsion. In "burning in" without water, heat lowers the surface tension sufficiently to give good penetration. As soft a product is not obtained because the fibers were not previously separated by water.

Further investigation should be done with the microscope to determine whether mineral oil acts like the animal and vegetable oils on microscopical sections of leather wetted by water. A method of photographing the penetration of oils in sections wetted by water would be very convincing. The difficulty at present is that oil wets the glass slide and cover-glass, in preference to, or as well as, leather. Great enough depth of focus cannot be obtained for photography to allow the use of uncovered specimens. Cow hide cannot be used for sections for photography since it is too tough to be cut into thin enough sections to make them sufficiently transparent or light enough in color.

Cornell University.

HELICOIDAL CONFIGURATION IN LONG-CHAIN COMPOUNDS

BY WILLIAM B. LEE AND PIERRE J. VAN RYSSELBERGE

In a previous paper[1] experimental evidence was adduced in favor of an helicoidal arrangement of carbon atoms in straight-chain carbon compounds, but the architecture of the helix was not defined. Our present purpose is to describe and discuss the spatial relationships of the carbon atoms in this definite and new helicoidal model, and to show that the theoretical deductions presented below are in very good agreement with a large number of experimental data relating to the most diverse properties, both physical and chemical.

There are already some existing theories[2 3 4 5 6 7 8] of the ordinary alternations in physical properties between odd and even members of the chain but they all omit to discuss the peculiarities we have observed at the 5th, 10th, and 15th carbon atoms in the chain. Moreover such theories differ fundamentally with respect to the mechanism which is responsible for these phenomena. Our treatment of the problem is more general and may include some of the earlier theories as special cases.

The tentative helicoidal model we have devised for palmitic acid (see below) has practically the same dimensions as those which Langmuir[9] deduced from N. K. Adam's measurements of monomolecular films on water. Likewise these dimensions are in fairly good agreement with the X-ray data.

A molecular model for straight-chain compounds should satisfy the following conditions:

1. The differences in physical properties between the odd and even members of homologous series must be shown by means of a spatial relationship.
2. C_5, C_{10}, C_{15} are specially characteristic points in many homologous series and the corresponding periodicity must be evident.
3. The first few members of homologous series have abnormal or greatly enhanced physical and chemical properties relative to all the rest which constitute the true family.
4. Five (and six)-membered rings are the most stable and the most readily formed.
5. The dimensions of the molecule must agree approximately with those deduced from X-ray measurements and from the study of monomolecular films of long chain compounds on water or mercury.
6. The same molecule must exist (at least potentially) both in the solid and liquid states.
7. The "alternations" between odd and even members should die away (a) with increase of temperature, (b) with increase of length of chain.*
8. Possibly, it is desirable that the tetrahedral angle should be retained—at least approximately.

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* Cf. Timmerman's convergence law: I. Simon: Bull. Soc. chimique de Belgique, 33, 47 (1929).

9. It should account for the optical activity of certain carbon compounds.

We believe that the helicoidal type of molecule is capable of satisfying most or all of the above requirements. Our theory of the carbon chain is based upon the following facts or principles:

(a) The "Spannung-theorie" of Baeyer, insofar as the 1-5 or 1-6 positions are the most favorable for ring formation.

(b) The first three or four members of homologous series exhibit anomalous or special properties which distinguish them from the higher members; together with the following assumption:

(c) Multiples of C_5 (C_{10} and C_{15}) are related to C_5 itself in much the same way as the harmonics of a note are related to its fundamental. It is not necessarily assumed that ring-formation is favorable at C_{10} and C_{15}, owing to the length of the chain; but that these positions have special significance in relation to other actions, e.g. *interfacial* action.

The plausible assumption (c) is found to receive strong experimental support, as is shown in the sequel.

The pitch of the helix is such that if all the C-atoms are arranged in two perpendicular planes, one complete turn of the helix has been made on reaching the 5th carbon atom. The somewhat special properties possessed by the first three or four members are due to the fact that the helicoidal form has not yet appeared; and, in contrast with this, all members from the fifth upwards form a true family with truly helicoidal molecules. For example, the first three or four members of the normal monobasic fatty acids have, relatively to the rest of the series, very high dissociation constants, di-electric constants, surface tension, esterification constants, etc. (together with particularly irregular melting points), whereas once the helix has been formed most of the above properties tend to settle down to a constant value. These are among the facts we seek to explain, which the ordinary plane "zig-zag" model of the X-ray investigator fails to do. Again, the action of the n-fatty acids on bismuth stops or cannot be detected by ordinary means at C_5; thereafter with increase of chain length the union at the interface metal-acid as in Hardy's lubrication experiments must be due to the formation of a kind of co-ordination or adsorption compound. The solubility of the n-fatty acids decreases extremely rapidly from an infinite to a very low value at valeric acid (C_5), and from Adam's experiments seems to disappear almost entirely at pentadecoic acid (C_{15}), whereas for practical purposes it is usually assumed that the acids become insoluble at about C_{10}.

It may be claimed that the helix is a *natural* geometrical form. It is particularly common in cylindrical structures in nature and is well illustrated for example in the spiral coil which stiffens the tracheal tubes of an insect, or the "tracheides" of a woody stem. (Right and left handed screw-axes afford an explanation for enantiomorphous crystals, such as those of quartz).

Pasteur (Leçons de Chimie, 1860) suggested that in the case of the tartaric acids we are possibly concerned with the properties of right and left-handed spirals or combinations of these. In recent years Astbury[10] has concluded from his X-ray studies that the carbon atoms in tartaric acid lie on a twisted spiral which forms the back-bone of the molecule. We predict that a similar result will be found in the X-ray study of the optically active long-chain compound, dihydroxystearic acid. Frankland[11] many years ago suggested that the carbon atoms of straight-chain compounds lie in a spiral or helix, and that corresponding to each turn of the helix we might expect a rough periodic recurrence of physical properties. That some kind of spiral (as opposed to a uniplanar "zig-zag") exists in homologous carbon series has also been emphasized repeatedly by Pickard and Kenyon[12] in connection with their classical investigations on the optical activity of carbon compounds. Donnan[13] has made reference to the possibility that the elastic compression of molecular helices could explain certain results obtained in the investigation of monomolecular films of long-chain compounds on water. Brigl and Fuchs[14] made the interesting suggestion that certain substances such as lignoceric acid (and certain of its derivatives), and fats with double melting points might have a kind of "spiral-staircase" structure. (They accounted for the special physical isomerism of lignoceric acid in this way.) Henderson,[15] Walker,[16] and others have hinted at the probability of the carbon chain being "spiral" in character as a result of their X-ray investigations of the normal saturated dicarboxylic aliphatic acids.

The Helicoidal Configuration

It is well-known that a cylinder is a developable surface and that (excepting two obvious cases) straight lines drawn on a plane become helices when this plane is rolled around the cylinder. Our assumption is that the carbon atoms of a straight chain lie on a helix drawn on a cylinder having the dimensions calculated by Langmuir[17] from Adam's measurements on monomolecular films. As a matter of convenience, we here use a circular cylinder, although it is probable that X-ray data may require, in some cases, an elliptical cross-section. The positions of the carbon atoms are regularly spaced around the cylinder (i.e. with respect to its cross-section), and the pitch of the helix is chosen in such a way that the odd and even carbon atoms lie respectively in two perpendicular planes. The positions so defined will be called the normal positions of the carbon atoms, but certain C-atoms, C_5, C_{10}, C_{15}, may easily leave their normal positions and come, in the extreme case, on another helix having a much larger pitch than the first one and constituting for the whole molecule a sort of "spinal cord."

In describing our model we take the case of palmitic acid for which measurements on monomolecular films and X-ray data are available. The cross-section of the molecule of $C_{16}H_{32}O_2$ and its length may be deduced from Langmuir's[17] calculations. We assume that the cross-section derived from the calculations is such that the carbon atoms are inside it. The cross-section passing through the centers of the carbon atoms is needed for the construction of the model.

The diameter of a carbon atom in diamond is 1.5 Å, approximately. Deducting this value from the diameter of a circle having the same area as the cross-section calculated by Langmuir, the diameter of the cylinder is 4 Å.

The height will be taken equal to 20 Å. The ratio of the height to the diameter is then 5:1, the value adopted by Langmuir. These dimensions agree rather well with the X-ray measurements of Müller[18] and Gibbs.[19]

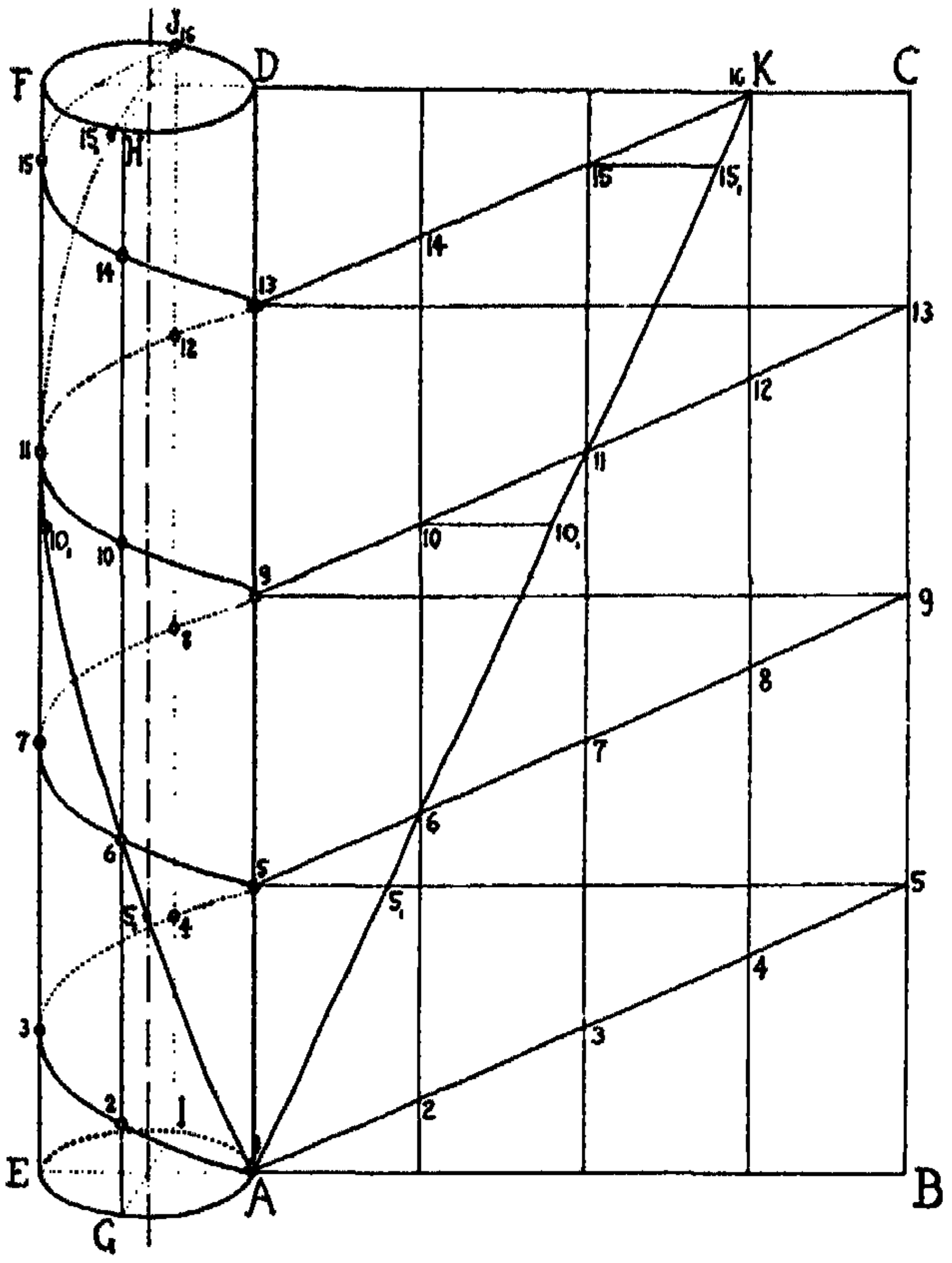

Fig. 1
Spatial Relations between the Carbon Atoms in a C_{16}-chain Compound, (e.g. palmitic acid).

Fig. 1 shows the cylinder and its development. Area of rectangle ABCD = area of curved surface of cylinder. AB is equal to the perimeter of the circular cross-section. C_1 occupies position A on the cylinder and on its development. C_{16} is at J. C_5, C_9, C_{13} are on AD when they occupy their "normal" positions; C_2, C_6, C_{10}, C_{14} are on GH, C_3, C_7, C_{11}, C_{15} on EF, C_4, C_8, C_{12}, C_{16} on IJ. It is easy to see that the height of the cylinder is equal to 5.75 times the pitch of the main helix. The development of this helix can be drawn. Going up from 1 to 13 the helix turns 3 times completely around the cylinder; from 13 to 16 we have 3/4 of one turn. The helix corresponding to the straight line 1-6-11-16 will play an important role in the explanation of the periodicity of the physical properties.

The configuration thus obtained corresponds to straight-chain compounds for which the ordinary alternation of properties between odd and even members exists. This configuration will be slightly modified for compounds presenting a second periodicity of the physical properties viz. at C_5, C_{10}, C_{15}.

Let us take first the case of valeric acid which has a melting point much lower than those of butyric and caproic acids. Going up from 1 to 4 no helicoidal properties appear. C_5 should come above C_1 and the configuration thus obtained is one turn of the helix. But, considering the well-known tendency of C_5 chain compounds to ring formation, we shall put C_5 in a position which renders it more independent of C_4 and which puts it under the influence of C_1, i.e. the position 5_1 on the helix 1-6-11. This helix exists in all the compounds of the series and constitutes a material representation of the 5-10-15 periodicity. The configuration 1-2-3-4-5 explains remarkably well, as will be shown later, the properties of valeric acid.

In chains having more than five carbon atoms it is possible that C_5 lies in its normal position, or a position intermediate between the normal one and the extreme position 5_1 on the helix 1-6-1, but this is not of fundamental importance for the present paper. It is probable, however, that in long chains which may form a 5-ring compound with a side chain, C_5 is very near the extreme position 5_1. We think also that the tendency to lactone formation depends also on the fact that certain carbon atoms are in abnormal positions in our helicoidal system. In the configurations previously proposed for the carbon chains it has usually been assumed that the angles between the lines 1-2, 2-3, etc. are very nearly equal to the tetrahedral angle 109°28′. In our model, with the dimensions chosen, this angle is equal to 100°40′ only, as is shown below by simple geometrical reasoning. It must be emphasized that the dimensions of our cylinder are only approximate and that a slight variation of its diameter has a great influence on the value of the angle. If the angle 1-2-3 must really be equal to 109°28′ the diameter of the cylinder can be changed accordingly[20,21]. The calculation of the angle 1-2-3 given below illustrates simply that our helicoidal configuration is not a random arrangement of carbon atoms but on the contrary has a real mathematical basis, that various modifications and extensions of the principles involved are possible.

Calculation of the Angle 1-2-3

Fig. 2 is a vertical projection of the chain 1-2-3 together with the corresponding horizontal projection. By a rotation of the plane 1-2-3 around a hortizontal axis passing through 1 and perpendicular to the vertical projection, we find the exact size of the triangle 1-2-3 in the hortizontal projection, $1^h 2^s 3^s$. We require angle α.

In the triangle $1^h\ 2^s\ 3^s$ or A B C we have:

$$\text{Cos}\ \alpha = \frac{AB^2 + BC^2 - AC^2}{2\ AB.BC} \qquad (1)$$

Calling p the pitch of the helix, tgφ its slope, d the diameter of the cylinder, we have:

$$\pi d \mathrm{tg}\varphi = p$$

But P = 20/3.75 = 5.33 Å
d = 4 Å
Thus tgφ = 0.424
In the triangle $1^{v}\ 3^{v}$ D we have $D3^{v} = p/2 = 2.66$ Å

$$Di^{v} = d = 4 \text{ Å}$$

$$\therefore 1^{v}\ 3^{v} = \sqrt{4^2 + 2.66^2} = 4.8 \text{ Å}$$

In ABC : $AC = 1^{v}\ 3^{v} = 4.8$ Å
$BC = 1/2.\sqrt{AC^2 + AE^2}$

But AE = d = 4 Å
Hence BC = 3.12 Å and AB = BC = 3.12 Å
Applying formula (1):

$$\mathrm{Cos}\,\alpha = \frac{2 \times 3.12^2 - 4.8^2}{2 \times 3.12^2} = -0.188$$

Hence α = 100° 40′.

It is therefore obvious that this angle may be changed, if desired, by a suitable adjustment of the magnitudes upon which it depends. Moreover, if the carbon skeleton lies on a long, narrow, elliptical cylinder this arrangement may lead to a plane zig-zag as an approximation.

With the pattern we propose it is obvious that molecules are in contact with each other along generating lines of their respective cylinders and that cohesion in the solid state results from the number of points of contact between contiguous molecules. These contacts exist between carbon atoms and we obtain a system of points corresponding to Tammann's[22] points of high lattice energy. Assuming further that in the n-fatty acid series C_5, C_{10}, C_{15} stay on the spinal cord on the molecule whatever the length of the molecule may be it is possible to calculate the number of these points of contact. It is easily seen that there are four possibilities for the arrangement between molecules: generating line 1 is in contact with generating line 1 of another molecule: 2 with 2, 3 with 3, and 4 with 4. A second possibility is 1 with 2 and 3 with 4. A third possibility is 1 with 3 and 2 with 4, and a fourth possibility 1 with 4 and 2 with 3. Other arrangements are mixtures of the foregoing. In this way we find that fatty acids exist in four different forms but that three of these forms have the same stability. If we consider now forms of the same stability as physically identical we come to the conclusion that even acids in the solid state exist in two forms, and we arrive at the same conclusion for odd acids but the stability of one of these forms being rather smaller than that of the other three, a smaller quantity of this form should be present. These conclusions agree with Tammann's ideas on this subject. It can be shown that the number of points of contact increases regularly with the total number of carbon atoms in the chain but inflections appear in the neighborhood of C_5, C_{10}, C_{15}. For instance, the number of points of contact for valeric acid is equal to that for butyric acid. This means that the cohesion in the solid state is relatively smaller than for butyric or caproic acid and that therefore a minimum melting point should be expected for this acid. This in fact is found to be the case. Our picture of the mechanism of the transition from the solid to the liquid state is somewhat as follows: The long-chain compound, say a normal fatty acid, is held in the space-lattice by the directed cohesive forces between individual molecules and the melting point is the temperature at which these cohesive forces are overcome by thermal agitation. In the liquid, especially near the melting point, a strong tendency to lattice formation exists; but there is an equilibrium between aggregations of molecules held together by the directed forces of residual affinity and the individual molecules. This equilibrium is very dependent on the temperature and on the length of the carbon chain. At higher temperatures, e.g., at the boiling point, a random distribution holds sway. The smaller oscillations of physical properties in the liquid state and their rapid decadence with increase of temperature are therefore due to the gradual departure from the space-lattice type of distribution. The soaps melt to anisotropic liquids and finally become isotropic at a higher temperature. However there must exist a *tendency* for the crystal lattice to form even in the isotropic state. The idea that fragments of the crystal space-lattice exist in the liquid state received support from the work of Tammann,[22] Beutler,[23] and recent investigations on the diffraction of X-rays by pure organic liquids. Beutler assumed that a liquid has a tendency to reproduce the crystal structure of the corresponding solid, and used this idea to account for the dying out of the oscillations with increase of temperature. The electronic explanation of Cuy[24] is of an entirely different character, but it accounts remarkably well for the alternations of properties between the odd and even members of the chain.

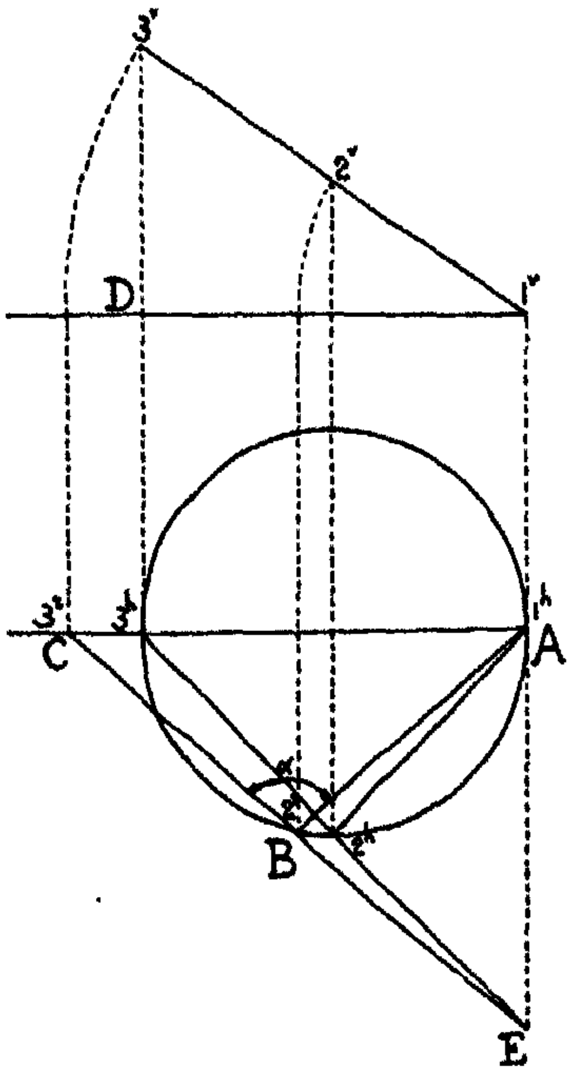

Fig. 2
Determination of the Angle $C_1C_2C_3$

A few applications of the helicoidal model to experimental data follow. The properties which we have investigated are grouped into three classes for convenience.

Group II lists some properties important in capillary and interfacial phenomena which appear to be intermediate between the so-called physical properties of Group I and the decidedly chemical properties in Group III. Only a few of the more important data will be given here as illustration.

I	II	III
Melting Point	Surface tension of *solutions*	
Boiling Point	Emulsifying agents	Dissociation constants
Molecular Volume	Monomolecular films	Velocity constants
X-ray data	(Spreading coefficient, surface pressure and electrical properties.)	Heat of neutralization
Dielectric constant	Work of adhesion	Complex molecular formation
Optical activity	Static friction	Esterification and Hydrolysis
Magnetic rotation	Heat of wetting	
Refractivity	Solubility	Ring formation
Heat of crystallisation	Foam stability	
Heat of combustion		
Viscosity		
Specific heat		
Surface tension of pure *liquids*		

For further details see a paper entitled: "Periodic Anomalies in the Properties of Long Chain Compounds," Trans. Faraday Soc., 33, Part 6 (1927).

Melting Point. Figs. 3 and 4 show the variations of M. Pt. with chain length for the n-paraffins, their related normal saturated fatty acids and primary alcohols, and the dibasic acids of the oxalic acid series. The alternation between odd and even members is well-known but attention is directed to the very pronounced minima in the M. Pt. curves for the n-fatty acids and the dibasic acids at C_5. There is also a tendency to a minimum at C_5 in the alcohol series, whereas this effect is practically non-existent in the paraffin series. The melting points also tend to a minimum at C_{10} and C_{15} in the n-fatty acid and alcohols, but this effect at C_{10} and C_{15} is again negligible for the paraffins. However the specific heats of the paraffins C_1 to C_{15} inclusive have been determined by the same investigator[25] over the range 0°-50° and there is a clear minimum at C_{10} which is outside the experimental error for these determinations. Summarising we may say that anomalies exist at C_5, and probably at C_{10} and C_{15}, in the properties of the solid crystal. The paraffin hydrocarbons in the solid state do not exhibit at all clearly the C_5, C_{10}, C_{15} periodicity whereas in the monobasic and dibasic acids, and alcohols, it is evident.

Boiling Points. For all the above series the "alternations" have almost died out at the boiling point. The only exception of importance is a distinct flattening of the curve at C_{15} in the B. Pts. of the n-fatty acids.

Molecular Volumes. The molecular volumes of the n-fatty acids at the M. Pt. alternate considerably as might be expected on our theory. The alternations of molecular volume fade away rapidly with increase of temperature as anticipated. In complete accord with this, Garner and Ryder[26] find that the molecular volumes at 50° C of the C_8, C_9, C_{10}, and C_{11} chain acids do not

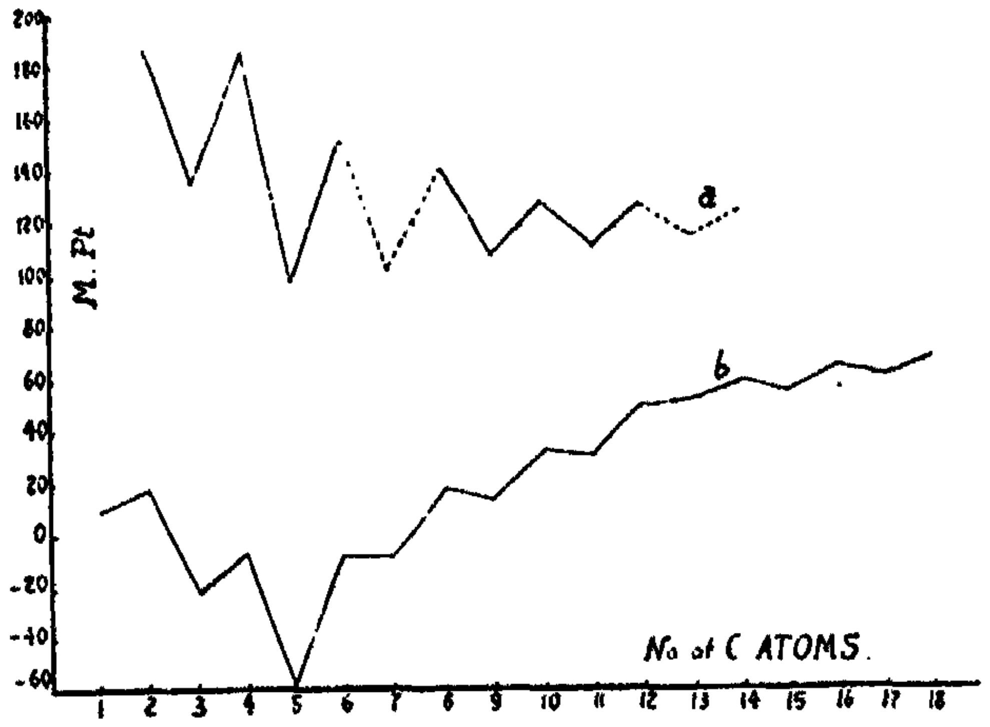

Fig. 3
Melting Point of
(a) Oxalic Acid Series
(b) N-fatty Acids.

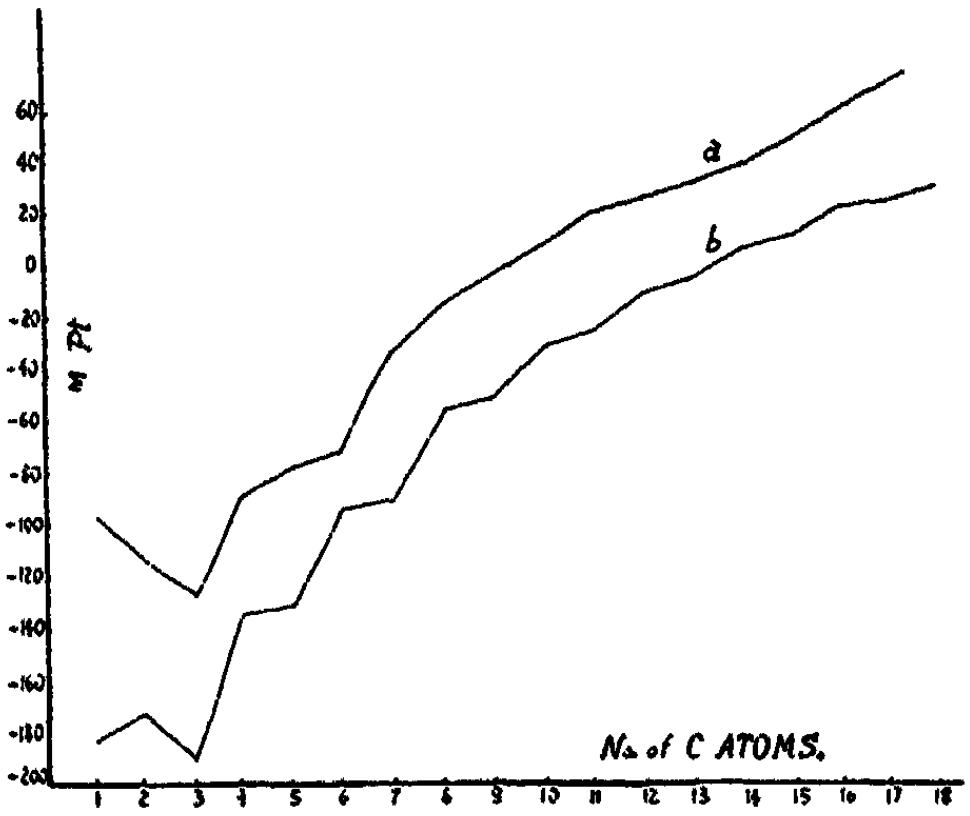

Fig. 4
Melting Point of
(a) Methyl Alcohol Series.
(b) N-paraffins.

alternate and if any fine distinction is to be drawn on the basis of their measurements the molecular volume tends to a minimum at C_{10}.

Surface Tension and Total Surface Energy. The results of Hunten and Maass[27] for the total surface energy (ergs) for 12 n-fatty acids are plotted in

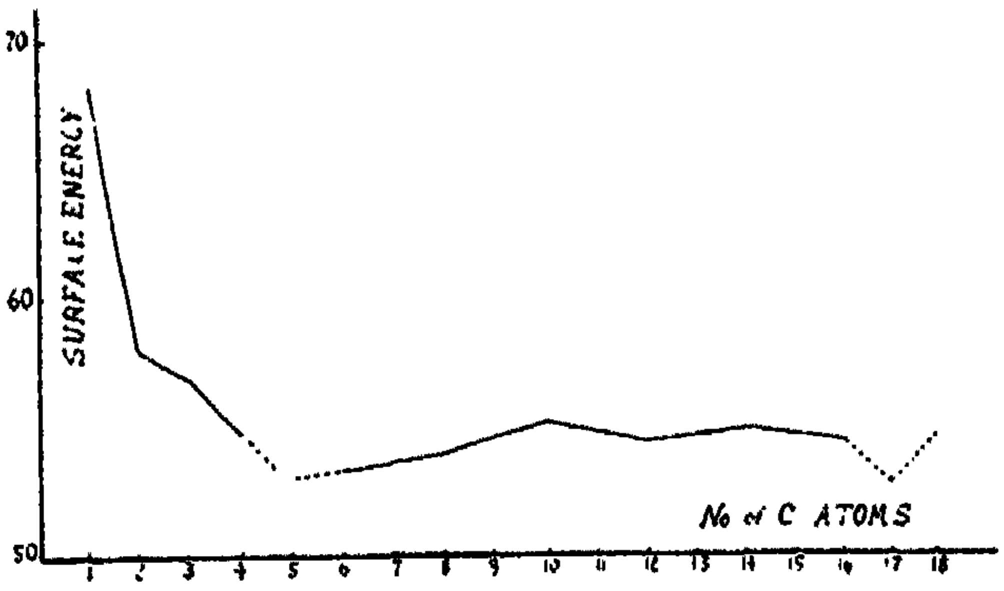

Fig. 5
Total Surface Energy of N-fatty Acids.

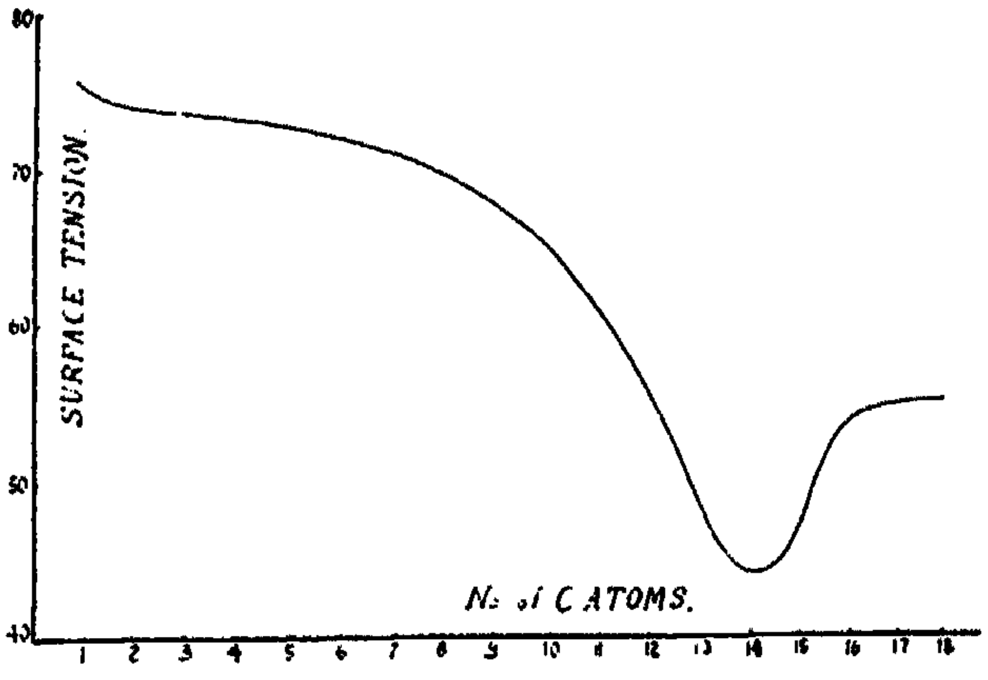

Fig. 6
Surface Tension of Equi-molar Soap Solutions
(Typical Curve obtained by Lascaray).

Fig. 5. What we call the "brake effect" of c_6 on the curve is clearly shown, i.e.: at C_6, the carbon helix begins to control the surface tension of the series. Here the change at c_5 is evident in the LIQUID state. Definite changes at C_{10} and C_{15}, may exist although this conclusion cannot be drawn with certainty here. In some earlier work, Drücker[28] found the internal pressure (both at 25° and at 35°) to diminish from formic to valeric acid. The internal pressure of the C_5 liquid acid *tends* to be somewhat lower relatively to C_1, C_2, C_3, C_4,

and this is to be expected if the lattice structure persists to some extent in the liquid state, for minimum cohesion in the liquid then corresponds to the minimum of M. Pt. of valeric acid.

The Surface Tension of Soap Solutions. Fig. 6 shows some of Lascaray's[29] results for the surface tension of equi-molar solutions plotted against molecular weight. For all such equi-molar curves a very striking minimum surface tension is found at C_{14} (sodium myristate). Here we have maximum adsorption and some fundamental change in the residual affinity of the molecule occurs at C_{14}, with a corresponding change in the electric moment of the interface air-adsorbed film. (Electrical measurements by Frumkin[30] of monomolecular films support this view). We see that the C_{15} soap here acts as a brake on the tendency of the soaps C_{10} to C_{14} to become abnormal with respect to the first 10 members of the homologous series. (A recent paper by Traube[31] states that the so-called Traube's rule according to which the surface tension lowering of homologous surface active substances in aqueous solution increases with increasing molecular weight in the ratio $1:3:3^2$ only holds to about the 9th term of a series and from the 10th term the solutions become surface inactive and the substance dissolves colloidally dispersed.)

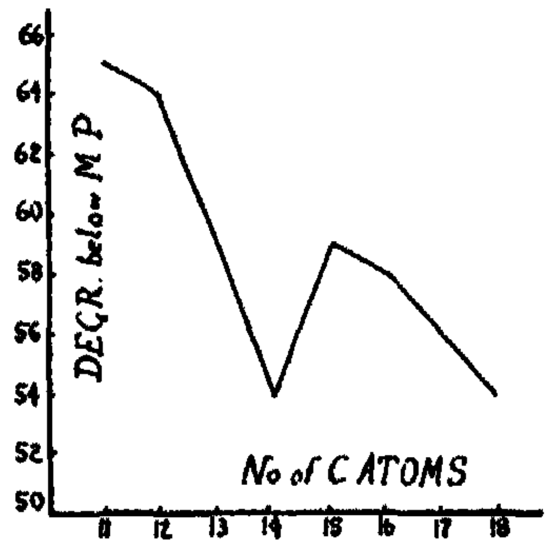

Fig. 7
Degrees below the Melting Point at which Surface Solution begins (N-fatty Acids).

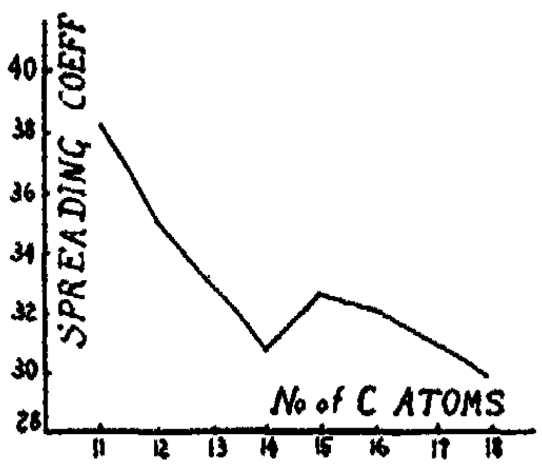

Fig. 8
Spreading Coefficient (at M.Pt.) of N-fatty Acids.

"Surface Pressure" and "Spreading Coefficients." The equilibrium pressures of the n-fatty acids (C_{11} to C_{18}) on water and their alternation with temperature were measured by Cary[32]. The ordinary fluctuations of bulk M. Pt. between the odd and even members are inappreciable or non-existent in these monomolecular films. He found that no measurable lowering of the surface tension of the water occurred until a well-defined temperature was reached. We have plotted Cary's results so as to show the number of degrees below the M. Pt. of the bulk phase at which "surface solution" begins against the number of C-atoms in the molecule. (Fig. 7) There is a striking minimum at c_{14}. A similar minimum occurs at C_{14} on plotting Cary's measurements of the spreading coefficients at the M. Pt. against molecular weight. (Fig. 8).

Work of Adhesion. An interesting application of our theory to interfacial phenomena, where one of the phases is solid, is to be found in the paper of Nietz,[33] who measured the work of adhesion of the n-fatty acids to water. (See Fig. 9). The odd members of the higher fatty acids can exist in two solid forms (α and β). The thick lines show the regular alternation between the even and α-odd forms. The upper dotted line is for the α-odd acids, the lower dotted line for the even and β-odd forms. The β-odd C_{15} and C_{17} members are indicated on special dotted lines. The work of adhesion shows a strong minimum in the region *C_{12} to C_{14}*. (Actually Nietz's lowest value is for C_{14}). The difference between an even and the next higher odd acid is attributed to a change in the crystal structure. Nietz says: "The general trend of the results however with a definite minimum in the neighborhood of C_{13} for the even acids and C_{12} for the α-odd acids and in particular the marked increase in the work of adhesion for the higher acids is entirely unsuspected and difficult to account for." Again, "it is believed that the effect of the length of the chain must in some part be responsible for the results obtained." We consider that Nietz's results constitute one of the best demonstrations of the configuration in space of the carbon chains. There is a sharp change in the residual affinity of the molecule due to its configuration at C_{14}. Here again C_{15} acts as a "brake."

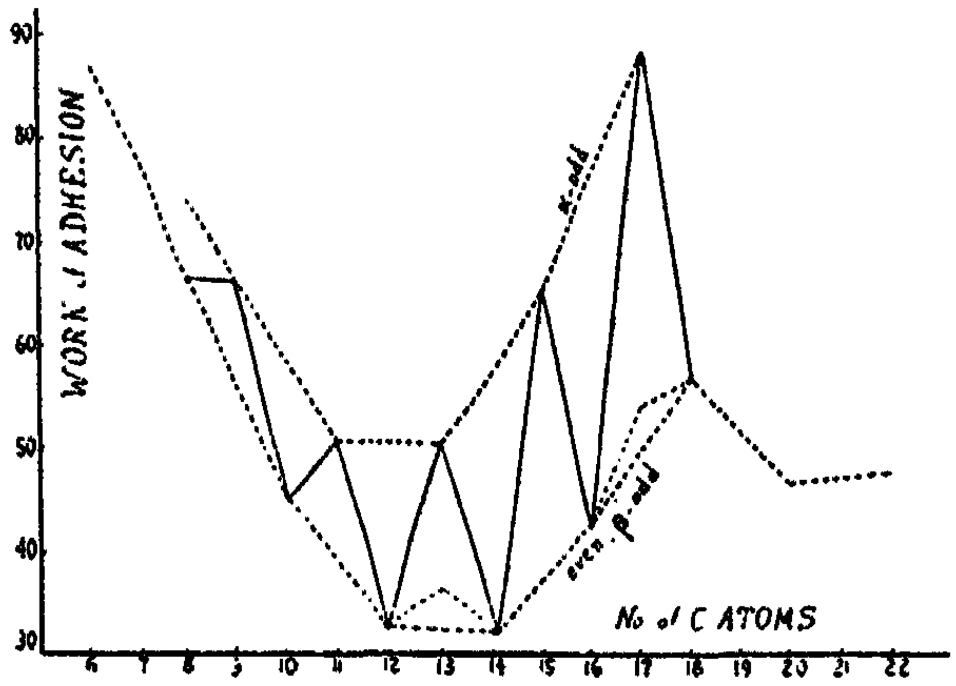

Fig. 9
Work of Adhesion of N-fatty Acids to Water.

Molecular Rotary Power. The following extract from a paper by Kenyon and Snellgrove[34] is significant in relation to our helicoidal configuration. "The specific and molecular rotatory power of ethylvinylcarbinol which are the highest of the series are in agreement with the prediction of Frankland (J. Chem. Soc., **75**, 868 (1889)) that some irregularity (maximum or minimum) in rotatory power might be shown by that member of a homologous series of compounds which contains five carbon atoms." "The result is analogous to that shown by d-methyl-n-propyl-carbinol in ethyl-alcoholic solution; the molecule of each of these alcohols consists essentially of a chain of five carbon atoms.

Dissociation Constants, Chemical Reactivity, etc. Fig. 10 shows Ostwald's[35] values for the dissociation constants of the lower normal fatty acids at 25°.

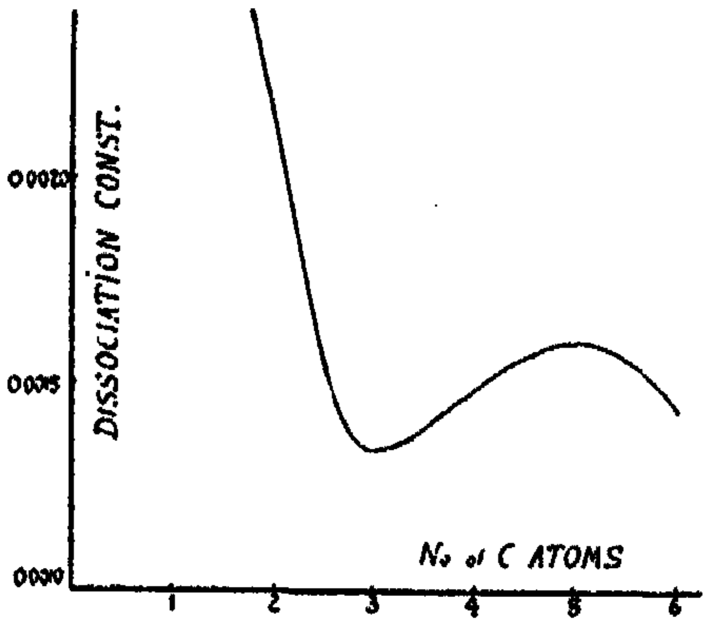

Fig. 10
Dissociation Constant of N-fatty Acids.

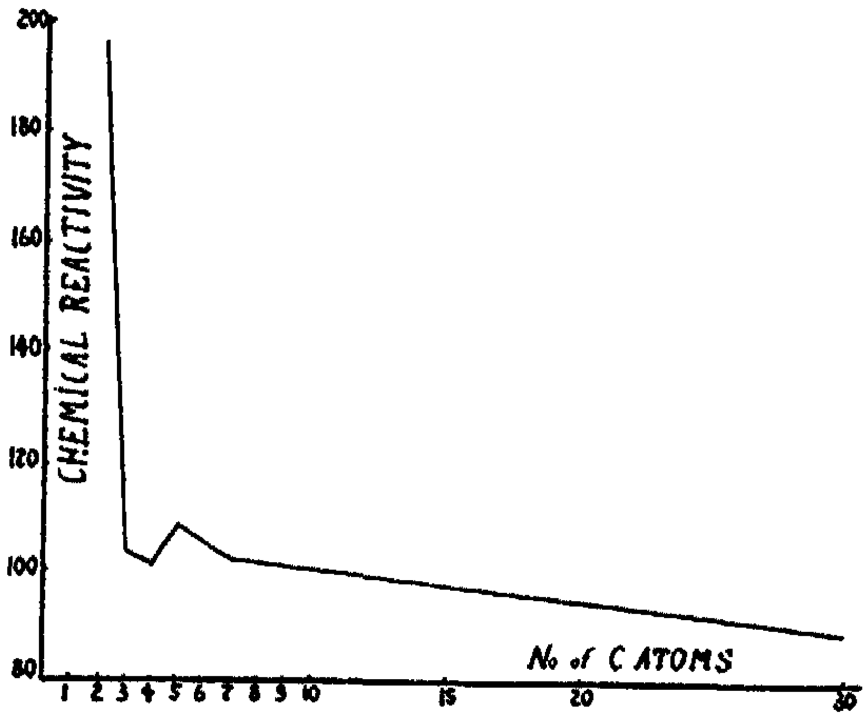

Fig. 11
Relative Chemical Reactivity of Alkyl Chlorides with Potassium Iodide.

Here the effect of C_5 is illustrated in solution. A fundamental relation naturally exists between the dissociation constants of the n-fatty acids, their spatial configuration, and the strength of the various bindings in the molecule. Several investigations of Sudborough[36] on esterification constants together with those of McBain and Hay[37] on the hydrolysis of soaps lend support to the view that myristic acid is a stronger acid than decoic, lauric, and palmitic acids. A corresponding effect is found at C_5 in the oxalic acid series. Fig. 11

illustrates the relative "chemical reactivity" of the alkyl chlorides in interaction with potassium iodide in absolute *acetone solution* at 60°C. (See Rice: "The Mechanism of Homogeneous Organic Reactions" (1928)). We use the term "chemical reactivity" here, as most chemists have done, in connection with the speed of the reaction rather than in relation to the extent to which a reaction proceeds. The relative chemical reactivity curve shows a maximum at C_5.

The ordinary alternation of physical properties between the odd and even members, even in the liquid state, is well-known and has been taken for granted. The 5-10-15 periodicity in the physical and chemical properties of the n-fatty acids and some derivatives has been illustrated in the crystal-lattice, the liquid state, and in solution. The relative importance of these positions in the chain depends upon the particular conditions or environment. It is facts such as the preceding which are accounted for by our helicoidal configuration of the molecule.

Summary

Assuming in principle the well-known theory of Baeyer relating to the ready closing of a chain of 5 or 6 carbon atoms, a new helicoidal configuration for long-chain compounds is derived and its mathematical basis is briefly illustrated.

It is then shown that this helicoidal model of the molecule accounts for many important physical and chemical properties. The dimensions of the molecule proposed for palmitic acid are of the same order of magnitude as those deduced from modern work in surface chemistry, and from X-ray data.

In addition to the well-known alternation of physical properties between odd and even members of the fatty acids, there is good evidence for a distinct, 5-10-15 periodicity. This periodicity is of fundamental importance in relation to the theory of chemical and interfacial actions and, in general, ordinary physical properties also tend to a maximum or minimum at C_5, C_{10}, and C_{15}. These remarks apply in the first instance to the normal fatty acids and the soaps, the normal dibasic aliphatic acids, and probably to certain other simple homologous series.

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[2] Cuy: Z. anorg. Chem., **115**, 273-287 (1921).
[3] Tammann: Z. anorg. Chem., **109**, 221-225 (1919).
[4] Stark: Z. anorg. Chem., **119**, 292-298 (1921).
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[6] Biach: Z. physik. Chem., **50**, 43 (1904).
[7] Nekrassow: Z. physik. Chem., **128**, 203 (1927).
[8] Beutler: Z. physk. Chem., **119**, 25 (1921).
[9] Langmuir: J. Am. Chem. Soc., **39**, 1848 (1917).
[10] Astbury: Proc. Roy. Soc., **102A**, 506 (1923); **112**, 53 (1923).
[11] Frankland: J. Chem. Soc., **75**, 868 (1899).
[12] Pickard and Kenyon: J. Chem. Soc., **103**, 1924 (1913).
[13] Donnan: Chemistry and Industry, **42**, 892 (1923).
[14] Brigl and Fuchs: Z. physiol. Chem., **119**, 286 (1922).
[15] Henderson: Proc. Roy. Soc. Edin., **1928**.
[16] Walker: Proc. Roy. Soc. Edin., **48**, 20 (1928).

[17] Langmuir: loc. cit.

[18] Müller: J. Chem. Soc., **123**, 2043 (1923).

[19] Gibbs: J. Chem. Soc., **125**, 2622 (1924). See also "International Critical Tables," **1**, 347.

[20] Müller (Proc. Roy. Soc., **120A**, 457 (1928) considers that the "zig-zag angle" in the single crystal of the hydrocarbon $C_{30}H_{62}$ is about 25° smaller than the tetrahedral angle.

[21] Walker (Proc. Roy. Soc. Edin. **48**, 20-27 (1928)) in an X-ray study of saturated dicarboxylic acids and amides of the fatty acid series has concluded that the angles between adjacent carbon atoms are not necessarily constant; but only approximately equal to the tetrahedral angle.

[22] Tammann: Z. anorg. Chem., **109**, 221 (1920); Z. physik. Chem., **85**, 273, (1913); Z. anorg. Chem., **115**, 288 (1920).

[23] Beutler: loc. cit.

[24] Cuy: loc. cit.

[25] Cf. "International Critical Tables," **5**, 107-113.

[26] Garner and Ryder: J. Chem. Soc., **127**, 722 (1925).

[27] Hunten and Maass: J. Am. Chem. Soc., **51**, 159 (1929).

[28] Drücker: Z. physik. Chem., **52**, 677 (1905).

[29] Lascaray: Kolloid-Z., **34**, 73 (1924).

[30] Frumkin: Z. physik. Chem., **116**, 485 (1925).

[31] Traube: Z. f. physik. Chem., **138**, 86 (1928).

[32] Cary: Proc. Roy. Soc., **109A**, 318 (1925).

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[34] Kenyon and Snellgrove: J. Chem. Soc., **127**, 771 (1925).

[35] Ostwald: "Outlines of General Chemistry," 120.

[36] Sudborough and Gittins: J. Chem. Soc., **93**, 211 (1908); Chem. Zentralblatt, **1926**, I, 80.

[37] McBain and Hay: J. Chem. Soc., (to be published shortly).

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April, 1929.

ENTROPY AND PROBABILITY

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It is well known that the entropy S of a gas is related to the probability W of the state of the gas by Boltzmann's relation;

$$S = k \log W + \text{Constant} \qquad (1)$$

where k is Boltzmann's constant. This subject has been treated by two methods. One is the method of collisions or kinetic method involving Boltzmann's H Theorem.[1] The second is the statistical method that consists in applying the laws of dynamics to determine the behavior of an ensemble of systems, each system itself composed of atoms and molecules, whose state is determined by their positions in phase space.[2]

The present paper is a new derivation of (1) and the known expressions for entropy and the chemical constants for different types of gas. The method is essentially distinct from (a) the method of collisions, and (b) the statistical method. On the one hand molecular impacts are never discussed. On the other hand phase space is never referred to (except for purposes of comparison) and no such inquiries are made into the behavior under dynamical laws of ensembles of systems of molecules in phase space as characterize statistical mechanics. The present method is thus not statistical as the term is used by Gibbs and Maxwell.

Furthermore there is no mechanics in the present treatment except that which is implicitly included in the probability axioms themselves. All the mechanics concerned with entropy is concentrated into these axioms which might properly be called:

Six Mechanical Axioms of a Priori Probability

I. The probability of a particle's having a position in ordinary space equals the probability of its having any other position in ordinary space.

II. The probability of a particle's having a position in velocity space equals the probability of its having any other position in velocity space.

III. The probability of a particle's having a position in momentum space equals the probability of its having any other position in momentum space.

IV. The probability of a particle's having one orientation equals the probability of its having any other orientation.

V. The probability of a particle's having a position in angular momentum space equals the probability of its having any other position in angular momentum space.

VI. The probability of a particle's having a position in action space equals the probability of its having any other position in action space.

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[1] Jeans: "Dynamical Theory of Gases," Chapters II, III.

[2] Gibbs: "Statistical Mechanics," Introduction; Tolman: "Statistical Mechanics," Chapter I.

The method of establishing (1) will be to build up from these probability axioms an expression for W the probability of the state of a gas, and substitute in (1) and show that the result has the characteristic properties of thermodynamic entropy. The procedure is characterized by elementary probability methods without regard to collisions, statistics, or mechanical laws. Emphasis is laid on geometric relations which are involved. The key note is to measure probability by the *range* of whatever type of space is being considered that includes a particle, treating each degree of freedom of each molecule separately. And then to take the product for all degrees of freedom for all molecules to get the probability of the state of the gas.

No. 1. The Probability Axioms are supported by Liouville's Theorem.

It is well known[1] that Liouville's Theorem implies that the volume in phase space that includes the points of a mechanical system does not change altho the bounding surface may do so, and that all microscopic states have the same probability for a given energy content. This leads to the familiar method of measuring thermodynamic probability by extension in phase space. (Gibbs: "Statistical Mechanics"). Thus for a small element:

$$dW = A(dp_1dp_2\ldots dp_ndq_1\ldots dq_n) \qquad (2)$$

where A is a proportionality factor and the p's and q's are the momentum and configuration coordinates that go to make up phase space. If N is the number of molecules, then n equals 3N, 5N or 6N according as we are treating with monatomic, diatomic or polyatomic molecules. The probability of a particular microscopic state of a gas as given by (2) according to Liouville's Theorem measures it by a volume element in phase space which element itself is nothing but the product of the elemental ranges of the three to six dimensional momentum or configuration space for all N molecules multiplied together. And this is precisely the product that would be obtained if each dimension of each molecule had its probability separately measured by the range dp_1 or dq_1 that includes it according to the above probability axioms and then the several probabilities multiplied together according to elementary theory as applied to independent probabilities. Thus the established method of measuring probability by extension in phase space is a necessary condition that follows from the probability axioms and the independence of a priori probability for each dimension of each molecule. The argument can also be traced backwards assuming independence of probabilities, and hence that for each dimension for a molecule the probability is measured by the range of momentum and displacement that includes it, and hence that the above axioms must hold and are a necessary as well as sufficient condition for measurement of a priori probability by extension in phase space.

Axiom VI is seen to be a generalization of the other five axioms and covers the situation where the momentum range and space range are considered together for each dimension.

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[1] Tolman: "Statistical Mechanics," Chapter III.

No. 2. Relativity and a priori Probability.

It is to be noted that the second probability axiom above is in accord with the principle of relativity. According to the special relativity the laws of nature take the same form when viewed in reference frames moving with different relative uniform velocities. Thus there is "democracy" among such frames in that one is not to be preferred over another. Thus if we consider particles travelling at different speeds, an observer travelling along with one of them in a moving reference frame, may rightfully consider himself "at rest" according to relativity. If no reference frame is to be preferred, the probability of a frame's having one velocity is equal to the probability that it will have any other velocity, and likewise with the particles that travel along with it. Thus Axiom II and Axiom III in like manner are supported by the special relativity.

The shortcomings of the Theory of Relativity in regard to rotations are well known and no attempt is made here to show the connection between it and the above probability axioms that deal with orientation and rotation. On the other hand it is shown in No. 10 that Axioms IV and V which imply the measurement of probability for internal degrees of freedom by orientation range and angular momentum range, are consequences of Axioms I, II, and III applied to measurement of probability of the constituent atoms in their courses about the molecular center of gravity, just as the ordinary mechanics of rotations follows from Newton's laws dealing with the translation effects.

It is noteworthy that the foregoing argument applies only to a priori probability (Type A, see No. 4) and not to probability of Type C given by (15) which corresponds to a Maxwellian distribution. Although such a distribution maximizes, as is well known, the a priori probability of Type A as shown in No. 9, yet it does so subject to the special condition that the total energy is constant, and this results in having more molecules within equal velocity ranges at one position of velocity space than at another, in seeming conflict with the *a priori* probability Axiom II. The relativity principle applies to the *a priori* situation to which no reference frame is related in a special way. The condition for a given total molecular energy related to temperature, or that the molecules are all included in a given volume, are local outside effects that modify the application of the *a priori* probability axioms and the relativity principle.

No. 3. The Ratio of the Probabilities of Two Temperature States of a Gram Molecule of Perfect Gas at Constant Volume is given when Equilibrium prevails in Terms of the Two Root Mean Square Velocities by:

$$W_o/W = (v_o/v)^{3N}$$

In this section we assume a Maxwellian distribution of velocities, corresponding to equilibrium conditions, and compare an equal amount of perfect gas (N molecules) at two different temperatures.

According to Maxwell's distribution law, it is well known that for a gram molecule of gas at a given temperature T the number of molecules with velocity components in the x direction between u and u + du is given by:

$$dN = \frac{N}{\sqrt{\pi}\,\alpha} e^{-(u/\alpha)^2} du = y\,du. \qquad (3)$$

where α is the most probable velocity corresponding to that temperature and is related to v the root mean square velocity by:

$$v = \alpha\sqrt{3/2}. \qquad (4)$$

If we plot $y = \frac{N}{\sqrt{\pi}\,\alpha} e^{-(u/\alpha)^2} = y_0 e^{-(u/\alpha)^2}$ (5)

against u the total area under the graph extending to infinity will evidently equal the number of molecules in a gram molecule:

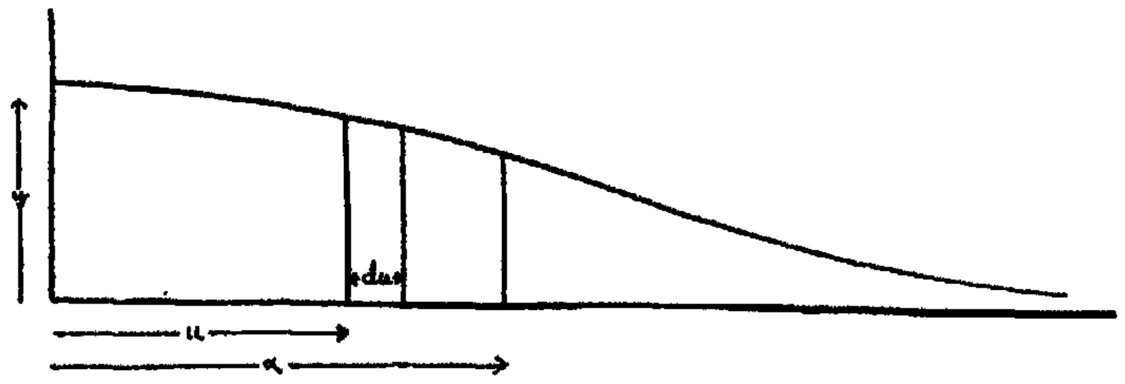

FIG. 1

Now graph a distribution for the same number (N molecules) occupying the same volume at a lower temperature T_0 taking note that the decrease in temperature increases the magnitude of the constant y_0 in (5) as well as reducing the denominator of the exponent of e:

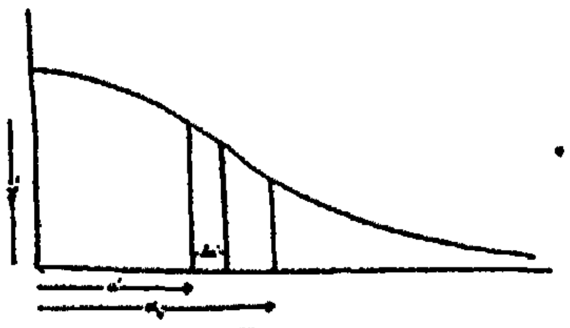

FIG. 2

Now fix attention on any variable u such as that shown in Fig. 1, and let it be related to the u′'s shown in Fig. 2 so as to make these two variables proportional to the corresponding constants α and α_0:

$$u/u' = \alpha/\alpha_0 \qquad (6)$$

If we consider only such variables u as satisfy (6), it is clear that the difference du between two of them is also related to the difference du′ between the two u's in the same proportion:

$$du/du' = \alpha/\alpha_0 \qquad (7)$$

If attention is turned to the y defined by (5) it is seen that the variable part (the exponential part) of y equals that of y′ to which it corresponds according to (6), whereas the constant coefficients of the exponentials are inversely proportional to the α's. Thus the y's will be inversely proportional to the α's to which they correspond according to (6):

$$y'/y = \alpha/\alpha_0 \tag{8}$$

Since $dN = dA = ydu$ and $dN' = dA' = y'du'$ we have from (7) and (8) at once that:

$$dN = dN' \tag{9}$$

provided the velocity limits between which the two groups of molecules of (9) are included correspond according to (6).

Since the functions are continuous we may integrate the differentials (9) between velocity limits that correspond by (6) and get:

$$M = \int_{u_0}^{u} ydu = \int_{u_0'}^{u'} y'du' = M' \tag{10}$$

where M and M′ represent the number of molecules for the cases of Fig. 1 and Fig. 2 respectively, included between *any* velocity limits *provided* that these limits correspond according to (6). Of course when the lower limits of (10) are zero and the upper limits are ∞ the correspondence (6) may still hold and then each M becomes N the Avogadro constant, since each case considered, refers to that number of molecules. Since the limits of (10) correspond by (6) we have in view of (4):

$$\frac{u - u_0}{u' - u_0'} = \frac{\alpha}{\alpha_0} = \frac{v}{v_0}; \tag{11}$$

Eq. (11) regarding the limits of (10) shows that *any* two *ranges* of velocities corresponding by (6) will include equal numbers of molecules and are proportional to the root mean square velocities corresponding to the two temperatures.

The reason for choosing velocities and velocity ranges that correspond by (6) is to make the number of molecules included between chosen velocity limits the same for the two gases at temperatures T and T_0 respectively, (or the same gas at different temperatures), according to (9) and (10). If the number of molecules is the same for the two gases between pairs of corresponding velocity limits, then since each gas is taken to include the same entire number of molecules N, it follows that the probability that a molecule among the N at temperature T shall be within a given velocity range, equals the probability that a molecule among the N at temperature T_0 shall be within the *corresponding* range. These probabilities, however, which are of Type C (see No. 4) refer to molecules already included among those at temperature T or T_0 and do not refer to the *a priori* greater probability (of Type A) that a molecule will be included among those at temperature T than among those at a lower temperature T_0 as is about to be shown. The true interpretation then for the equalities (9) and (10) is then as follows: If a molecule is among those N at temperature T and another molecule is among those N at temperature T_o then the probability (of Type C) that the first molecule be included within any range of velocities, is equal to the probability (of Type C) that the other molecule be included within the range of velocities that correspond by (6). In other words, barring differences in a priori probability (Type A) that a molecule be amongst those at temperature T or T_o, the probabilities (of Type C) are equal that it be included between velocity ranges that correspond by (11) for the two temperatures. This means that if we fix attention on molecules that are included between ranges of velocities that correspond by (11) then the *only* differences in probability will refer to *a priori* probability (Type A) that they be among those at one or the other of the temperatures in question. Thus we may investigate the comparative probabilities of two temperature states.

In accord with the elementary fact, Axiom II, noted at the outset of this paper, the a priori probability of a molecule's occupying one position in velocity space will equal that probability for any other such position. Thus for the x component of velocity, u, the molecule is as likely to be represented by one position along the horizontal range from 0 to ∞ in Figs. 1 and 2 as by any other position—that is, apart from the superimposed temperature conditions represented by those graphs. Accordingly, the probability of a molecule's being within one range of velocities as compared with the probability of its being within another range is in direct ratio to the extent of the two velocity ranges, just as the comparative *a priori* probabilities of a molecule's being within two linear space ranges are directly proportional to the extent of the two ranges. Instead of considering any two velocity ranges, let us fix attention on the two ranges of (11) which include equal numbers of molecules and whose velocity limits correspond to each other by (6). The probabilities that a molecule will be within one or the other of the ranges indicated satisfy the ratio:

$$\frac{W}{W_o} = \frac{u - u_o}{u' - u_o'} = \frac{v}{v_o} \tag{12}$$

If the ranges of velocities given by (11) are extended indefinitely taking the lower limits $u = u' = 0$, and representing the upper limits by the infinity symbol, and maintaining the correspondence (6) during the extension process, the relation (12) still holds while the range of velocities includes in each case the total number N of molecules considered for the two temperatures T and T_o. Thus the comparative probabilities that one molecule will have a u amoung the N molecules at temperature T, and that it will have a u′ among the equal number at T_o are proportional to the root mean squares of the agitation velocities at the two temperatures as shown by (12). Likewise, with the y and z components of velocities. We assume in accord with the fundamental principles of probability mentioned at the outset of this paper and as usual in kinetic theory, that the probabilities of x, y and z components of velocities are independent of one another. Then the comparative probabilities that one molecule will have the three components of its velocity among the velocities of those N molecules at temperature T and that it will have them among the equal number at T_0 are proportional to the product of three ratios like (12), one for each dimension:

$$W/W_0 = (v/v_0)^3 \tag{13}$$

If we consider a perfect gas or elastic sphere which has only three degrees of freedom, then the above three velocity components completely determine the kinetic energy state of the molecule. Hence (13) gives the comparative probabilities that one molecule will have a kinetic energy state like those included among the N molecules at temperature T shown in Fig. 1, and that its energy state will be represented among those N molecules at temperature T_0 shown in Fig. 2. For two independent molecules the comparative probabilities will be given by the square of (13) and for N independent molecules we have:

$$W/W_0 = (v/v_0)^{3N} \tag{14}$$

for the comparative probabilities that N molecules will all have their energy states represented by the N molecules at temperature T shown in Fig. 1, and that their states will be like those of the N molecules at temperature T_0 shown in Fig. 2. This amounts to saying that (14) gives for perfect gas (three degrees of freedom) the comparative probabilities that N molecules will be at temperature T and that they will be at temperature T_0, assuming that they occupy equal volumes.

No. 4. The Three Types of Probability of a Molecule's Energy State.

If two different bodies of the same type of gas have N molecules and N′ respectively, and occupy equal volumes and are at the same temperature, then the probability that a molecule will be included in the one gas compares with the probability that it will be within the other in proportion to the number of molecules, since all other factors are equal. We refer to this type of probability which depends on the numbers of molecules involved as Type B probability.

A different though related type of probability is given by the familiar Maxwell distribution function:

$$\frac{dN}{N} = \frac{1}{\sqrt{\pi}\,\alpha} e^{-(u/\alpha)^2} du \tag{15}$$

which we refer to as Type C Probability.

It is to be noted that in the last section the two temperature states of gas whose graphs were compared, referred to the same number N of molecules in each case. This was purposely done so as to rule out consideration of Type B probability. The method of the last section also restricted attention to molecules included within velocity ranges that 'corresponded' according to (6). This also was done purposely so as to rule out of consideration Type C Probability given by (15) for it is readily seen from (7), (8) and (9) that (15) is the same for velocity ranges that correspond according to (6).

Thus the only type of probability which in the last section was not ruled out of consideration (with reference to the velocity or energy state of the gas) is the type which depends on and is measured by the *range* of velocities that include the molecules considered. We refer to this as Type A Probability, and take note that this is the *a priori* type of probability that depends on Axiom II stated at the outset of this paper, and corresponds for velocity space to the elementary probability which is measured by ordinary space or volume range.

No. 5. Entropy Differences for a Gram Molecule of Perfect Gas.

If W and W_o of (14) are substituted in (1) and the constant removed by subtraction we have:

$$S - S_o = k \log (v/v_o)^{3N} = R \log (v/v_o)^3 = R \log (T/T_o)^{3/2} \qquad (16)$$

for entropy differences at constant volume for a gram molecule of gas with three degrees of freedom. Since the ratio of the probabilities for a particle that it will occupy volume V or V_o is given by V/V_o according to Axiom 1, we may, assuming independence of probabilities, multiply this ratio raised to the Nth power by (14) and obtain:

$$W/W_o = (v/v_o)^{3N} (V/V_o)^N \qquad (17)$$

for the comparative probabilities that N molecules will occupy a volume V in ordinary space at the same time they occupy a range in velocity space corresponding to T, as compared with occupying volume V_o in ordinary space together with a range corresponding to T_o in velocity space. Here again if we substitute the W's of (17) in (1) and subtract, there results:

$$S - S_o = k \log (v/v_o)^{3N} (V/V_o)^N = R \log (T/T_o)^{3/2} (V/V_o) \qquad (18)$$

which is the general expression for entropy differences per gram molecule. If we take $S_o = 0$ and add the constant from which entropies are measured (18) takes the familiar form for perfect gas:

$$S = R \log (T^{3/2}V) + \text{constant}. \qquad (19)$$

No. 6. Real Gases and Symmetry Numbers.

In comparing probabilities of states of perfect gas reliance is based solely on Axioms I and II since differences in mass do not enter. In case of real gases, however, where the measure of probability depends on extension in momentum space, the analysis must rely on Axiom III since Axiom II does not apply except as between molecules of the same mass.

Axiom IV is not concerned with monatomic molecules because only one orientation is possible in a physical and mechanical sense for an elastic sphere. A diatomic molecule, on the other hand may have different orientations where its axis of symmetry ranges through a solid angle 4π. If, however, it is a symmetric diatomic molecule composed of two identical atoms, its solid angular range for 'different' orientations in the physical sense is reduced by one-half. Thus for diatomic molecules $4\pi/\sigma$ may be taken in all cases to measure the angular range ($\sigma = 1$ or 2) of possible orientations.

With polyatomic molecules we may take any axis through the center of gravity and get in general different orientations while this axis ranges through a solid angle 4π like the axis of the diatomic molecule. Not only so, but the unsymmetric polyatomic molecule will when turned about this axis, in any particular position, give a succession of new orientation states corresponding to a rotation through an angle 2π. Thus $2\pi.4\pi = 8\pi^2$ is the angular range for the unsymmetric polyatomic molecule. In general, the angular range for the orientation states of the polyatomic molecule is given by $8\pi^2/\sigma$ where σ is the symmetry number of the molecule. Thus for Methane (CH_4) with an H atom at each corner of a tetrahedron, the angular range is $8\pi^2/12$, since the symmetry number is 12. (Four symmetric axes could be chosen, and in rotating around any one of these, three positions of symmetry are found).

No. 7. Thermodynamic Probability, Weight, Action Range.

We have heretofore discussed comparative probabilities only, because the denominator of the probability ratio is unknown. We now fix attention on the numerator, having regard to the third law of Thermodynamics which implies minimum unit probability at the absolute zero if Boltzman's equation (1) still holds in that region. Thus if the minimum probability is unity to which others are referred, the numerator of the probability ratio will actually be the thermodynamic probability, and when substituted in (1) gives the absolute value of the entropy without the added constant there shown, because the only required constants would then be involved in the probability expression itself.

The uncertainty in regard to the exact mathematical expression for thermodynamic probability makes it desirable from the point of view of rigor to introduce some exactly defined quantity which shall be proportional to the probability throughout the domain of physics under discussion, which in the present instance, is restricted to gases with fully excited degrees of freedom. Ehrenfest has felt so strongly this need for rigor with reference to so elusive a quantity as thermodynamic probability that in a recent paper by him and Trkal[1] the word probability does not appear at all. We shall follow these authors in defining 'weight' as the numerator of the probability ratio, to which the probabilities of the states of the gases here considered are proportional. The present definition of weight, however, is based on the foregoing six axioms of probability and is the action range of one or more molecules, according as we consider the weight of one or more molecules of gas. Although approached from a different angle, this definition of weight is fundamentally the same as that of the above authors, since the foregoing axioms are in accord with the results of Liouville's Theorem which affords the basis of the definition of weight given by Ehrenfest and Trkal. We rely on this proportionality between probability and weight to extend the application of the probability axioms and thereby compare the entropy and the states of different types of gas having different numbers of molecules, instead of restricting attention as in No. 3 to comparisons between gases having in each case the same number of molecules.

This extended application of these probability axioms requires a more refined definition of 'range' than previously used. For ordinary space, the three dimensional range is the volume occupied by the gas. But this may

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[1] Ann. Physik, (4) 65, 609 (1921).

be analyzed by taking the reciprocal of the density $1/n$, the volume occupied by one molecule as the range of a particular molecule. And this range measures the weight or probability of the volume state of this molecule. But there are N molecules which are equally likely to be within this volume so that N times the volume $1/n$ is the weight that measures the probability that a molecule will be within this volume. Thus $N(1/n) = V$ is the weight per molecule. And the weight for N molecules so far as their position in ordinary space is concerned is V^N, being the product of N weights corresponding to the N molecules.

By analogous reasoning we define the range of a molecule at a particular place in velocity space, as the reciprocal of the number of molecules included in unit length of velocity space there. Just as the above n is a continuous function taken in this case to be constant, so in velocity space the distribution function is taken to be a continuous function so that the definition of range above given involving the reciprocal of the distribution function (See No. 8) is uniquely determined everywhere throughout velocity space. Likewise the momentum range per molecule is uniquely defined throughout momentum space. And the action range per molecule is also defined uniquely for each dimension throughout action space, and is the product of the range per molecule in ordinary space and the range per molecule in monentum space.

No. 8. The Maxwellian Distribution of Velocities is most probable.

We may assume an unknown and continuous velocity distribution function referring to N molecules:

$$dN = N\,f(u)du \tag{20}$$

which gives the number of molecules between the velocity limits u and u + du. Then:

$$dN/du = N\,f(u) = 1/r \tag{21}$$

is the number in unit velocity range at position u in velocity space. The reciprocal of (21) gives the distance there in velocity space between successive molecules in the x direction:

$$r = \frac{1}{Nf(u)} = u_{j+1} - u_j. \tag{22}$$

and it is this length in velocity space which we take according to No. 7 to define the range of a particular molecule at this position in velocity space, and it is the weight that measures the corresponding probability. If there are N molecules and all are equally likely to be in the range in question, then the probability that one of them will be in this range is N times (22):

$$w = \frac{1}{f(u)} \tag{23}$$

which gives the weight per molecule where the velocity is u. If the N molecules are alike and have constant x component of total energy we have the restricting constant:

$$E_x = \tfrac{1}{2}m(u_1^2 + u_2^2 + \ldots\ldots + u_N^2 \tag{24}$$

where the u's are the x components of the agitation velocities of separate molecules. Thus the weight that measures the probability that a molecule will be in the ith. range corresponding to (23) is

$$w_i = \frac{1}{f(u_i)} \tag{25}$$

Since the probability that a molecule will be in one range is independent of the probability that it will be in any other range, we have for the total weight the product of N such expressions as (25):

$$W = \frac{1}{f(u_1)\, f(u_2) \ldots\ldots f(u_N)} \tag{26}$$

where the u's are independent variables except for the restriction (24). Now apply the Lagrange method for conditional maxima and form the function where λ is an arbitrary constant:

$$F = W + \lambda E. \tag{27}$$

and take the partial derivatives for N independent variables:

$$\frac{\partial F}{\partial u_1} = -W \frac{d}{du_1} \log f(u_1) + \lambda m u_1 = 0 \tag{28}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\frac{\partial F}{\partial u_i} = -W \frac{d}{du_i} \log f(u_i) + \lambda m u_i = 0$$

where it is readily seen that the first term on the right is the partial derivative of (26). If $W/m\lambda$ is eliminated between any two or more of these N eqs. we have:

$$\frac{d/du_1\,(\log(f(u_1)))}{u_1} = \ldots\ldots \frac{d/du_i(\log(f(u_i))}{u_i} \ldots\ldots\ldots = m\lambda/W \tag{29}$$

The u's determined by (28) and (29) are a set of constants that give the maximum value of W. If we set the right member of (29) equal to $-2b$ then these N constants must all lie on the curve whose differential equation is:

$$\frac{d}{du} \log f(u) = -2bu. \tag{30}$$

Integrating:

$$f(u) = c\, e^{-bu^2} = \frac{1}{\alpha\sqrt{\pi}} e^{-(u/\alpha)^2} \tag{31}$$

we get the distribution function, a curve on which all the u's determined by (28), (29) must lie, where on the right the constants are expressed in terms of α the most probable velocity being related to temperature in the usual manner. When f(u) given by (31) is interpreted in connection with (20), (21) and (22) it is seen to determine a unique set of constant values (the abscissas shown in Fig. 3) of the u's that give the maximum value of W. Thus we may plot (20) taking $y = N f(u) = \frac{N}{\alpha\sqrt{\pi}} e^{-(u/\alpha)^2}$ as ordinate and u as abscissa, and then equal areas correspond to equal numbers of molecules, and we obtain the area corresponding to each molecule if we divide the total area into N equal areas by parallel ordinates as indicated:

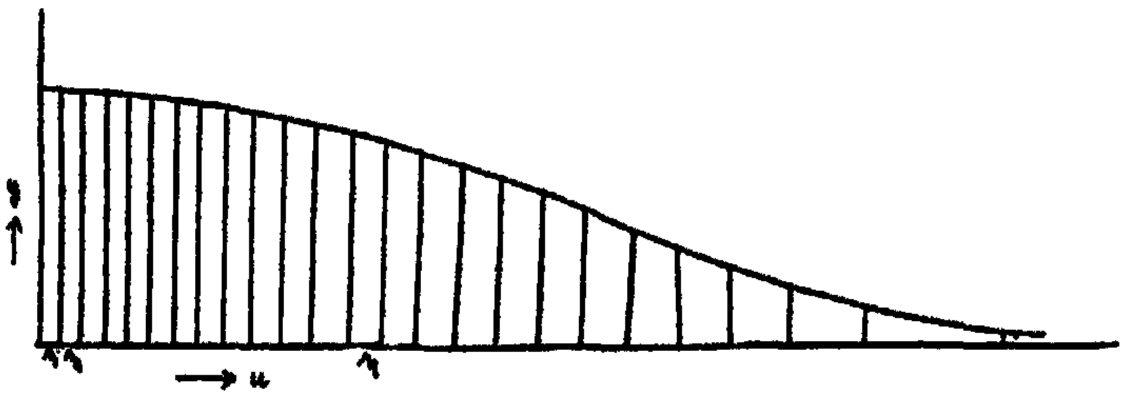

Fig. 3

The base of these areas is the r given by (22) corresponding to the molecule at that place in velocity space, and the sum of i of these r's starting from the left gives the velocity u_i of the ith molecule to the same approximation that a continuous velocity distribution fits a gas of finite number of molecules. Although the finite number of equations (29) does not uniquely determine the differential equation (30) involving the continuous variable u, yet the number of u's involved in (29) can be increased indefinitely till all possible values of u appearing in (30) are represented. Thus the distribution function (31) is uniquely determined since N the number of ordinates shown in the graph (the number of molecules) may vary indefinitely without altering the form of (29), (30) and (31).

The same result is obtained if we take account of (22) and express W as a product of differences between successive u's:

$$W = N^N \pi_{i=1}^{N} (u_i - u_{i-1}) = N^N (r_1 r_2 \ldots\ldots\ldots r_N). \qquad (32)$$

This is the same identical W as given by (26) expressed explicitly in terms of the u's. Now use the Lagrange method for conditional maxima with this W and form the F corresponding to (27) and take the partial derivatives as (28) and obtain equations corresponding to (29):

$$\ldots\ldots = \frac{\partial/\partial u_i \log (u_i - u_{i-1})(u_{i+1} - u_i)}{u_i} = \ldots\ldots = 2b. \qquad (33)$$

These N equations may be solved for the N constants $u_1 \ldots\ldots u_N$ which determine the maximum of (32). On the other hand we may take

$$(u_i - u_{i-1})(u_{i+1} - u_i) = (r_i)^2 \qquad (34)$$

as the square of the difference of velocities between successive molecules at the place u_i in velocity space, to the same approximation that a continuous function represents a distribution of a finite number of molecules. Then in view of (34) and (22), (33) is the same equation as (29) (when the arbitrary constants are adjusted), so that the velocity differences of (33) correspond to the velocity distribution law (31) and the set of u's given by (31) is the same as that of the distribution law shown in Fig. 3.

An advantage is gained by expressing W as (26) in terms of the undetermined distribution function f(u) instead of the equivalent explicit form (32) in that we obtain the distribution function directly as the condition for maximum probability, and this distribution function is the essence of the problem and itself of course uniquely determines the set of u's that give the maximum value of W.

Although we have here only shown that (31) satisfies the necessary condition (28) for the maximum of W it is well known that the Maxwell distribution is the one of maximum probability and satisfies the sufficiency condition also. Thus it may be shown that $\partial^2 W/\partial u_i^2$ is negative by taking W in the form (32) and letting u_k be the dependent one of the N variables resulting from the condition (24). Then the first and second partial derivatives of u_k with respect to u_i are readily obtained from (24) and when these are substituted in $\partial^2 W/\partial u_i^2$ and account taken of (33) where b is positive, the resulting expression is seen to be negative according to the requirements of the sufficiency condition.

No. 9. The Maximum Probability for a Distribution of Momenta.

Formula (26) gives the weight for one dimension of a velocity distribution of N molecules. It is based on Axiom II and measures the weight for a molecule by its velocity range, and combines them by multiplication. More generally we have seen according to Axiom III, that as between different types of molecules the probability and hence weight is to be measured by the momentum range. Thus we may proceed just as in (8) using a distribution of momenta like (20) instead of velocities and obtain the weight of the distribution in one dimension of momentum space instead of (26):

$$W = \frac{1}{f(p_1)f(p_2)\ldots\ldots f(p_N)} \tag{35}$$

This expression of course does not include the probability of distribution in ordinary space. If we evaluate this formula for the equilibrium state of maximum probability as treated in No. 8, we have for f(p) the Maxwell distribution function:

$$f(p) = \frac{1}{(2\pi mkT)^{\frac{1}{2}}}\, e^{-(p_x/p)^2} \tag{36}$$

which when substituted in (35) gives:

$$W = (2\pi mkT)^{N/2}\, e^{(1/p)^2(p_1^2+p_2^2+\ldots.p_N^2)} = (2\pi mkT)^{N/2} e^{E_x/kT} \tag{37}$$

where E_x is the x component of the total energy of agitation. If we note that $E_x = NkT/2$ we can write (37) in the form:

$$W = (2\pi emkT)^{N/2} \tag{38}$$

If all molecules had the same momentum range it would be for a certain average molecule and is given by the Nth root of (38):

$$W = (2\pi emkT)^{\frac{1}{2}} = \sqrt{\pi e}\ m\alpha = (2\pi mkT)^{1/2}\, e^{kT/2kT} \tag{39}$$

which is readily seen from (23) and (36) to be the momentum range of the molecule whose energy is $kT/2$ and hence whose velocity is the root mean square velocity for the distribution (36).

$$\tfrac{1}{2}m\alpha^2 = kT;\ v^2 = 3/2\alpha^2. \tag{40}$$

Remembering that every molecule has $kT/2$ for its average energy per degree of freedom, we see that (39) is the momentum range of every molecule when in its average energy state, and this is very properly referred to as the weight per molecule per translational degree of freedom, so far as momentum state is concerned and as *the* momentum range per molecule.

No. 10. The Weight of Monatomic, Diatomic and Polyatomic Gas.

Since the velocity distributions in the *y* and *z* directions are similar to the velocity distribution of *x* components, the expressions for the weight that measures the probability state of the other two distributions of momenta components will be the same as (38) and (37) except that E_x is replaced by E_y or E_z. And the product of these three gives the weight for the three translational degrees of freedom so far as momentum is concerned. If we multiply this product by V^N we obtain the total weight for the three translational degrees of freedom as the product of the space range V by the momentum range (39) of the molecule with mean energy, all raised to the Nth power:

$$W_m = V^N(2\pi mkT)^{3N/2}\,e^{E/kT} = V^N(2\pi emkT)^{3N/2}. \tag{41}$$

which is the weight that measures the probability (at its maximum) of a distribution of N monatomic molecules in volume V at temperature T.

For diatomic and polyatomic molecules we have to consider the momentum range and space range involved in the internal degrees of freedom. These ranges may be calculated from Axioms I, II, and III without reliance on Axioms IV and V, by considering separately the space range and translational momentum range of each atom about the molecular center of gravity. Thus $2\pi r_1$ would be the space range of an atom (atom number 1) of a diatomic molecule in the circular path about the molecular center of gravity (r_1 being the distance of the atom from this point), as the molecule rotated about an axis normal to its own axis. And also just as in No. 9, (39) in the form $\sqrt{\pi e}\, m_1\alpha_1$ gives the translational momentum range along this circular path of the atom with corresponding mean translational energy. And the product of these two ranges gives:

$$w_1 = 2\pi r_1\sqrt{\pi e}\, m_1\alpha_1 \tag{42}$$

the action range of one atom (in the average energy state) about the molecular center of gravity for one degree of freedom. If we add to (42) the action range of the second atom at distance r_2 from the center of gravity of the diatomic molecule we get the total action range for one internal degree of freedom of the diatomic molecule: Likewise for the second internal degree of freedom for the first atom:

$$w_2 = 2r_1\sqrt{\pi e}\, m_1\alpha_1 \tag{43}$$

Here the space range involved is $2r_1$ instead of $2\pi r_1$ since the atom is not always at distance r_1 from the axis of rotation of the second internal degree of freedom but varies between this distance and o according to the position in the orbit of the first internal degree of freedom, and in such a way as to make the range $2r_1$. If we add to (43) the corresponding expression for the other atom we obtain the total action range for the second internal degree of freedom (for the atom with mean energy). If these two action ranges are multiplied together we get the total action range for the two internal degrees of freedom together:

$$
\begin{aligned}
w_i &= (2\sqrt{\pi e}\, m_1 r_1 \alpha_1 + 2\sqrt{\pi e}\, m_2 r_2 \alpha_2)\,(2\pi\sqrt{\pi e}\, m_1 r_1 \alpha_1 + 2\pi\sqrt{\pi e}\, m_2 r_2 \alpha_2) \\
&= (2\sqrt{2\pi e}\, I\omega)\,(2\pi\sqrt{2\pi e}\, I\omega) = 4\pi(\sqrt{2\pi e}\, I\omega)^2 = 4\pi(2\pi e IkT). \qquad (44)
\end{aligned}
$$

Here $(r_1\omega)^2 = \alpha_1^2/2$ is one third the mean square velocity corresponding to v in (40) and likewise with the second atom. Also $\frac{1}{2}I\omega^2 = kT/2$. The above expressions show the action range of the two internal degrees of freedom of the diatomic molecule (in average energy state). The first form gives it in terms of linear space ranges and translational momentum ranges of the separate atoms about the molecular center of gravity and was calculated from Axioms I, II and III. The last form gives it as the product of 4π the orientation range of a diatomic molecule (See No. 6) and the square of $(2\pi e IkT)^{\frac{1}{2}}$ which latter is the angular momentum range for the molecule in its mean energy state per degree of freedom, being the same as (39) except that I replaces m. The last form is thus the same as would have been obtained by relying solely on Axioms IV and V and multiplying the orientation range 4π, by the angular momentum range above obtained directly like (39) in No. 9 from the most probable distribution of angular momenta. Thus (44) illustrates that the angular momentum range and orientation range for internal degrees of freedom can be calculated directly from reliance on Axioms IV and V or indirectly by applying Axioms I, II, and III to the treatment of atomic space ranges and translational momentum ranges about the molecular center of gravity, in much the same way that the ordinary mechanics of rotation, torque, etc. can be established by application of Newton's laws to the translational effects concerned in the rotations. Since it is always possible to obtain the expressions like (44) from applying Axioms I–III to translational momenta, etc. or on the other hand by applying Axioms IV and V to rotational effects, we see that the latter axioms are supported by the first three axioms and follow as a consequence from them.

When the weight per molecule for the two internal degrees of freedom given by (44) is raised to the Nth power and multiplied by (41) taking M instead of m for the mass of diatomic molecule, we get the total weight for N diatomic molecules including translational as well as rotational degrees of freedom:

$$W_d = [4\pi/\sigma\ V(2\pi ekT)^{5/2}M^{3/2}I]^N \qquad (45)$$

Here the symmetry number σ generalizes the formula to take care of the symmetric diatomic molecule. (See No. 6).

The calculation of the weight for the internal degrees of freedom of the polyatomic molecule is like that for the diatomic molecule. We may rely on Axioms I, II, and III and calculate the space and momentum range of each atom separately in its course about the molecular center of gravity and combine as done for the diatomic molecule to get the internal action range which turns out again to be the product of the orientation range for the polyatomic molecule: $8\pi^2/\sigma$ by the angular momentum ranges for the three rotational degrees of freedom, just as if reliance had been placed on Axioms IV and V, and the angular momentum range calculated as in No. 9 for the molecule in average energy state given by the formula corresponding to (39):

$$w_i = 8\pi^2/\sigma(2\pi e I_1 kT)^{1/2}(2\pi e I_2 kT)^{1/2}(2\pi e I_3 kT)^{1/2} \tag{46}$$

Each of the radicals appearing in (46) can be obtained exactly as (39) was in No. 9 except that the p's of that section are to be replaced by angular momenta for one of the three degrees of internal freedom, and the corresponding relation between rotational energy and temperature is used. When (46) is raised to the Nth power and multiplied by (41) to include translational degrees of freedom, we have the total weight for N polyatomic molecules in terms of the action range of the molecule in average energy state:

$$W_p = [8\pi^2/\sigma\ V(2\pi ekT)^3 M^{3/2}(I_1I_2I_3)^{1/2}]^N \tag{47}$$

No. 11. Entropy and Weight.

To obtain the expressions for entropy of monatomic, diatomic and polyatomic gas, we substitute (41), (45) and (47) respectively for w in (1). The constant of (1) must then be retained since these expressions for weight only purport to be proportional to thermodynamic probability. Thus taking N as the Avogadro number:

$$S_m = R \log [V\ (2\pi emkT)^{3/2}] + C = R \log [V\ (2\pi mkT)^{3/2}] + E/T + C.$$

$$S_d = R \log [4\pi V/\sigma\ (2\pi ekT)^{5/2}M^{3/2}\ I] + C = R \log [4\pi V/\sigma\ (2\pi kT)^{5/2}M^{3/2}\ I] + E/T + C. \tag{48}$$

$$S_p = R \log [8\pi^2 V/\sigma\ (2\pi ekT)^3 M^{3/2}(I_1I_2I_3)^{1/2} +] C = R \log [8\pi^2 V/\sigma\ (2\pi kT)^3 M^{3/2}(I_1I_2I_3)^{1/2}] + E/T + C.$$

Here the second expression for entropy in each equation is obtained by replacing $R \log e^{i/2}$ (where i is the number of degrees of freedom) by its equivalent E/T where E is the total energy.

No. 12. Incorporation of the Quantum Theory.

It is to be noted that Axioms II, III, V and VI conflict with the quantum theory if they are interpreted as being exact, according to what seems to be the requirement of the relativity principle, as explained in No. 2. The whole theory herein, however, which is built upon the foundation of Axiom VI (which includes the other axioms) can be made to fit the quantum theory exactly if we shift the foundation on which it rests so that Axiom VI which is that foundation, will exactly fit the quantum theory perhaps at the expense of its exact adjustment to the relativity principle. Thus the revised form of Axiom VI would be:

Axiom VI[1]*: The Probability for each Degree of Freedom that a Molecule will have Action equal to a Given Multiple of h is equal to the Probability that it will have Action equal to any other Multiple*[1] *of h.*

Here *h* is Planck's action constant, and it is understood that only integral multiples of *h* are permitted. For large scale phenomena this Axiom and the others which depend on it will evidently approximate very closely the above theory and application of Axiom VI throughout this paper. It will be immediately seen that according to this Axiom VI[1] the probability or weight is measured not by the *range* of *action* or momentum (for each degree of freedom) but by the *number* of multiples of h involved in that range, since only integral multiples of h are admissible. Thus if $\sqrt{\pi e}$ max is the action range per molecule for one translational degree of freedom, then $\sqrt{\pi e}$ max/h is the weight or probability to be assigned to it, since this is the number of integral multiples of h that it involves. It will be observed that the above weight is a pure number since the numerator is action as well as the h. Although the method of obtaining the above action range from Maxwell's distribution law would not in general give a range that was an integral multiple of h (in view of the method of averaging quantities that may be taken to be multiples of h), yet any little proper fraction of h left over after dividing $\sqrt{\pi e}$ max by h would be negligible compared to the approximations to the quantum theory involved in Maxwell's distribution law. Thus for each degree of freedom we have instead of (39) the weight:

$$w^1 = \frac{\sqrt{\pi e}\ \text{max}}{h} \tag{49}$$

The expressions for weight (41), (45) and (47) will be adapted to the quantum theory according to (49) when the action range for each degree of freedom is divided by h. Then the measure of the weight will no longer be the action range, but the number of multiples of h included in that range, which is comparatively speaking a very close approximation to the previous expressions, although absolutely the change is significant, in that weight is now measured by a pure number, instead of an action range:

$$W_m = \frac{(V(2\pi emkT)^{3/2})^N}{h^3} \tag{41'}$$

$$W_d = \frac{(4\pi V}{\sigma}\frac{(2\pi ekT)^{5/2}M^{3/2}I)^N}{h^5} \tag{45'}$$

$$W_p = \frac{(8\pi^2 V}{\sigma}\frac{(2\pi ekT)^3}{h^6}M^{3/2})(I_1I_2I_3)^{1/2})^N \tag{47'}$$

No. 13. The Chemical Constants.

When these quantized expressions for weight are used in (1) instead of using the previous (41), (45) and (47) we have for the entropy of a gram molecule of each type of gas:

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[1] This is in accord with Planck's recent suggestion: Z. Physik, (4) 35, 155 (1925). See also Tolman: "Statistical Mechanics" section 394.

$$S_m = R \log [V \frac{(2\pi e m k T)^{3/2}}{h^3}] + C = R \log (VT^{3/2}a_m) + \frac{E}{T} + C.$$

$$S_d = R \log [\frac{4\pi V}{\sigma} \frac{(2\pi e k T)^{5/2}}{h^5} \sqrt{M^3 I^2}] + C = R \log (VT^{5/2}a_d) + \frac{E}{T} + C. \quad (50)$$

$$S_p = R \log [\frac{(8\pi^2 V}{\sigma} \frac{(2\pi e k T)^3}{h^6} \sqrt{M^3 I_1 I_2 I_3}] + C = R \log (VT^3 a_p) + \frac{E}{T} + C.$$

In the right hand members the so-called 'chemical constants' are represented by the a's:

$$a_m = \sqrt{m^3} \left(\frac{\sqrt{2\pi k}}{h}\right)^3$$

$$a_d = \frac{4\pi}{\sigma} \sqrt{M^3 I^2} \left(\frac{(\sqrt{2\pi k}}{h}\right)^5 \quad (51)$$

$$a_p = \frac{8\pi^2}{\sigma} \sqrt{M^3 I_1 I_2 I_3} \left(\frac{\sqrt{2\pi k}}{h}\right)^6$$

These results agree with the expressions for the chemical constants given by Ehrenfest and Trkal[1] (who introduce an extra *k* since pressure is used instead of volume in the entropy formula, and their notation is different). See also Tolman[1]: Statistical Mechanics, eq. 317.

No. 14. The Relation of Planck's Characteristic Function and Summation State of a Molecule to Entropy and Action Range.

The writer has not attempted to show that the expressions (48) are characterized by the properties of thermodynamic entropy, because it is well known that the entropy of gas in the equilibrium state of maximum probability is given by the right members of (48). Thus the entropy of a gram molecule of gas is given in the form:[2]

$$S = R \log Z + E/T + C = \psi + E/T + C. \quad (52)$$

where Z is the part included inside the logarithm of the right members of (48) and is known as the "Zustandsumme" after Planck, or summation state of the molecule, being the result of carrying out the integration indicated by his "Zustandsintegral." Thus for example, in case of monatomic gas we have:

$$Z_m = V(2\pi m k T)^{3/2} = \int e^{-\epsilon^2/\alpha^2} dp_x\, dx dp_y dy dp_z dz \quad (53)$$

Planck's "Characteristic Function" is also shown in (52) and is seen

$$\psi = R \log Z = -(E - ST/T) = -A/T. \quad (54)$$

to be related as indicated by (54) to Gibb's function A = (E−ST). Thus the form of (48) is in accord with well known entropy theory.

We may compare the summation state given by (53) with the action range of the monatomic molecule for three degrees of freedom (in its average energy state) given by the Nth root of (41). This action range is seen to

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[1] Ann. Physik, 65, 609 (1921); also Tolman: "Statistical Mechanics," Chapter III.

[2] Handbuch der Physik, 10 (Article by Schroedinger).

be the product $Z_m e^{3/2}$, i.e., the summation state multiplied by the square root of e, once for each degree of freedom. Likewise for the diatomic and polyatomic molecules, it is readily seen that the summation state multiplied by the square root of e, once for each degree of freedom, gives the action range for the five or six dimensions in the form of the Nth root of (45) or (47). We may examine this relation in more detail by dropping the V from (53) and then extracting the cube root, thus considering only that part of the summation state that refers to momentum in one dimension. If this is multiplied by the square root of *e* we have like (39):

$$w = (2\pi e m k T)^{1/2} = (2\pi m k T)^{1/2} e^{kT/2kT} = e^{1/2} \int_{-\infty}^{+\infty} e^{\frac{-u^2}{\alpha^2}} dp_x \qquad (55)$$

which shows that the summation state for one dimension of momentum is to be multiplied by the square root of *e* to give the momentum range of the molecule in its average energy state per degree of freedom.

Note that the part of the "Zustandsintegral" on the right of (55) represents a momentum range that is weighted by multiplication with the exponential, and that this weighting factor is thruout the integration always between 1 and 0 in magnitude. This naturally reduces the momentum range that the integral represents below the average and so this has to be offset by multiplying it by $e^{1/2}$ (greater than 1) to bring it up to the range of the molecule in its mean energy state as given by (55).

Thus in every case Planck's summation state Z is to be multiplied once for each degree of freedom by the square root of *e* to give the action range and hence the weight defined in the present paper. And furthermore, the weight so obtained gives the entropy when substituted for W in (1), (in the cases of maximum probability here treated) where the substitution of Z gives Planck's characteristic function.

No. 15. Comparison of the Geometrical Expression for Weight with the Statistical Expression for Weight.

The expressions for weight (26) and (32) may be shown equivalent to the more familiar expression used in statistical mechanics:

$$W = \frac{N!}{n_1!\, n_2! \ldots\ldots n_k!} (\omega_1)^{n_1} (\omega_2)^{n_2} (\omega_3)^{n_3} \ldots\ldots (\omega_k)^{n_k}. \qquad (56)$$

Here the ω's are small volumes in "μ-space" (of 6 to 12 dimensions according as we refer to molecules with three or six degrees of freedom) including the corresponding number n of molecules. And their product (when each is raised to the indicated power) gives the elementary volume in so called γ-space which is known as the geometrical part of the weight given by (56). The numerical coefficient involving the factorials of the n's is the statistical part and indicates the number of distinct arrangements in this γ-space. We may compare (56) with (26) and (32) the more simply if we restrict the ω's to one dimension say of velocity space, and then they will refer to a velocity range including the corresponding n molecules, which we can refer to as s. If we use the approximation:

$$\log N! = N \log N - N. \tag{57}$$

then the statistical part of (56), i.e., the factorials is readily seen to be equivalent to: $N^N/(n_1^{n_1}n_2^{n_2}\ldots\ldots n_k^{n_k})$, so that (56) can be written:

$$W = \frac{N^N}{n_1^{n_1}n_2^{n_2}\ldots\ldots n_k^{n_k}} (s_1)^{n_1}(s_2)^{n_2}\ldots\ldots(s_k)^{n_k}. \tag{58}$$

which refers like (26) and (32) to the weight of N molecules for one dimension in velocity space. Now it is noteworthy in connection with this theory that the ω's (and hence the s's) are entirely arbitrary, (except that in the quantum theory they are integral multiples of h) and it is in connection with this fact that the present treatment differs from the statistical one, for the prevailing mode is to choose the ω's as all equal (or at least constant) and then it is easy to employ the familiar method used by Boltzman of maximizing W with total energy constant and thereby derive the Maxwell-Boltzman distribution law. It is equally permissible, however, to keep the n's constant and let the ω's which are the geometrical part of (56) vary instead of Boltzman's method of keeping the ω's constant and letting the statistical part, i. e., the n's vary. And in particular we may take each n equal to unity, thereby removing the statistical aspect entirely and then if we refer to (58) instead of (56) the s's which correspond to the ω's will be the range in velocity space corresponding to the separate molecules, that is, the very r's given by (22) which were used in deriving the geometrical expressions for weight (26) and (32). Thus it is readily seen that (58) reduces to the right member of (32) when we take $s_i = r_i$ and $n_1 = n_2 = n_3 \ldots = n_k = 1$. We thus see why (26) and (32) are geometric, i.e., since the variable vital part is the geometrical action range including each particle. On the other hand the variable vital part of (56) and (58) is statistical being the n's, necessarily integers associated with arbitrary constant compartments of μ-space.

In the quantum theory the ω's of (56) are replaced by $g_i = m_i h$, integral multiples of h, which correspond to the energy levels for different quantum states in μ-space. The prevailing mode of keeping the ω's or g's constant and maximizing W by varying the n's, requires the variation of W to depend on quantities which are intrinsically integers since each refers to a particular number of molecules. It seems more appropriate physically to keep the n's constant (and each equal to unity as above) and let the ω's vary (by multiples of h in the quantum theory). This suggests that perhaps the quantum aspects of action and energy might be traceable behind some physical misconception to the intrinsic integral nature of distinct numbers of particles like the n's of (56) which perhaps should have the quantum aspects of some experiments attributed to them rather than to the ω's.

More generally the equivalence of (56) (26) and (32) appears in that each when substituted for W in (1) gives the same expression for entropy of gas in the equilibrium state. Thus:

$$S = k \log W = k(N \log N + N \log \omega - \sum_i n_i \log n_i) \tag{59}$$

Here we have used Sterling's approximation (57) (and the last term cancels off), and all of the ω's of (56) have been taken equal to ω and of course the sum of the n's equal to N. Now use the distribution law in the form: $n_i = N\omega/Z\ e^{-(\epsilon_i/kT)}$ corresponding to the equilibrium state, where Z is the summation state given by (52) and ϵ_i is the energy of the molecules in the compartment ω of phase space then:

$$\begin{aligned} S &= k(N \log N + N \log \omega - \sum_i n_i(\log N + \log \omega - \log Z - \epsilon_i/kT.)) \qquad (60) \\ &= R \log Z + E/T + C. \end{aligned}$$

which is the same as (48), (50) and (52). Altho we have relied on Sterling's approximation (57) to show the relation between (56) and (60), it is well known that this is not necessary but merely easy and convenient. Likewise the equivalence of (56) and (26) and (32) is general and the same physical expression for weight can be given either (following Boltzman) as the product of equal ranges (ω's) including different numbers of molecules, or as the product of different action ranges each including a single molecule as treated herein.

No. 16. Advantages of the Present Treatment.

The advantages of (a) the method of collisions, and (b) the method of statistical mechanics are well known. In contrast to these it is to be noted that there is no kinetics involved in the present treatment. And yet it is in accord with mechanics, since the axioms themselves are mechanical axioms. Secondly the present treatment involves no statistical mechanics except where the axioms are compared with Liouville's Theorem, and where the statistical expression for weight is compared with the new geometrical expression in the last paragraph. All reference to phase space, or inquiries into the behavior of ensembles of systems of molecules under dynamical laws is absent. Once the axioms are laid down to build on, the subsequent procedure is free from statistical[1] (as that term is used by Gibbs and Maxwell) or mechanical inquiries.

A notable departure is made in concentrating all the mechanics that applies to the subject into the Six Mechanical Axioms of A Priori Probability, and then in building on these by elementary probability methods, where the key note is to measure probability by the range that includes each particle, doing it separately for each degree of freedom of each molecule, and taking the product to get the probability of the state of the gas. Since the vital point about the present treatment is measurement of probability by variable range that includes each individual particle, rather than by variable numbers of particles included in arbitrary fixed ranges, it seems to be essentially a geometrical rather than a statistical method.

The writer is specially indebted to Prof. G. E. Uhlenbeck of the University of Michigan for valuable criticism and discussion: and also to Prof. Slater of Harvard for valuable criticism.

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[1] See Gibbs: "Statistical Mechanics," Introduction, also Tolman: Chap. I.

SUPERHEATING AND THE INTENSIVE DRYING OF LIQUIDS*

BY SAM LENHER

In connection with work on the intensive drying of liquids, the writer has had occasion to investigate some of the conditions which favor superheating of liquids. It was found that dried liquids boil at the normal boiling point when superheating is effectively prevented.[1] The experiments described in this paper will show that ordinary liquids can be superheated an amount equal to the rise in boiling point attributed by H. B. Baker to intensively dried liquids,[2] or liquids subjected to electrical potential,[3] under as nearly as possible his experimental conditions.

The conditions favorable to superheating in boiling point measurements are of more general interest than actual degree of superheating, for superheating, being an unstable condition, is not quantitatively reproducible. The first condition, and one which is too well known to discuss here, is the position of the thermometer in a boiling point measurement. When heating is carried out with a bath (as in Baker's experiments[4]) it is almost impossible to prevent superheating when the temperature is measured on a thermometer immersed in the liquid. The writer has heated purified benzene (boiling point 80.2° measured in the vapor) in flasks and tubes of different shapes using from 5 to 20 cc. of benzene, with the thermometer bulb immersed in the liquid, and boiling points as high as 106° have been obtained. In these experiments the vessels were open to the air and were not sealed by tubes dipping in mercury as in Baker's experiments. The vessels and the thermometer were carefully cleaned before an experiment. Boiling, when it began at the elevated temperature, was sometimes quiet and regular, and was sometimes violent. It was found that liquid which had been boiled once, and was air-free, could be superheated more than the unboiled liquid.

In one instance it was possible to reproduce an apparatus in which intensive drying was carried out by Smits[5] and in which an elevated boiling point was deduced. This apparatus is described as follows:[6] "Two wide tubes, A and B, 2 cm. in diameter, each containing two thermometers, one for reading the temperature of the liquid and the other for reading that of the vapour, were connected by a tube 1½ cm. wide in H-form." In the present experiment ordinary pure benzene was used without any drying

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* Contribution No. 18 from the Experimental Station of E. I. du Pont de Nemours and Co.

[1] Lenher and Daniels: Proc. Nat. Acad. Sci., **14**, 606 (1928).

[2] H. B. Baker and M. Baker: J. Chem. Soc., **101**, 2339 (1912); H. B. Baker: **121**, 568 (1922); Smits: **125**, 1074 (1924).

[3] Baker: J. Chem. Soc., **1928**, 1055; Smits: **1928**, 2407.

[4] Baker: J. Chem. Soc., **121**, 568 (1922).

[5] Smits: J. Chem. Soc., **125**, 1074 (1924).

[6] Smits: J. Chem. Soc., **125**, 1071 (1924).

agent. The apparatus was carefully cleaned. The following quotation from Smits paper (1924) gives some of his observations on dried benzene in this apparatus:

"During the distilling of the boiling benzene, the temperature of the liquid rose to 86.6°, whilst the temperature of the vapour was 81.8. There was still one-quarter of the original quantity of the liquid, but the bulb of the lower thermometer was no longer covered by the liquid. The distillation was continued and when nearly one-eighth of the original liquid was left, the temperature of the vapour had risen to 87.7°. If I could have determined the temperature of the small quantity of the liquid which was still boiling, it would certainly have been nearly 89°. . . . During this visit Professor Baker was kind enough to sacrifice, at my request, a small fractionating flask of dried benzene, in order to see if, as I had already predicted, a separation of the pseudo-components by distillation could be realized. There was a thermometer in the vapour only and although the liquid was evaporated, before boiling had begun, the temperature of the vapour rose from 81° to 87°.

"This experiment showed that distillation effected a separation of the pseudo-components.

"The experiments made in my laboratory and described above confirm the results obtained in co-operation with Professor Baker, and moreover they prove that this result can be obtained after one year of intensive drying."

The writer has observed the same phenomena in this apparatus with ordinary benzene. The tube containing benzene was heated slowly in a Nujol bath. As the bath was heated, the temperature of the liquid rose slowly from 80° to 90° over a period of thirty minutes with no sign of boiling, or bubble formation; the temperature of the vapor remained at 80.2°. On further heating the temperature of the vapor rose slowly over a period of twenty minutes to 89.5°C. There was evaporation from the surface of the benzene, and the vapor distilled and refluxed, but the liquid did not boil. The bath was well stirred, and the apparatus was tapped and even shaken with no appearance of boiling. Finally, after an hour's heating, the temperature of the liquid was 90°, while the temperature of the vapor was 89.5°. As the temperature of the bath was 110°, or 20° higher than that of the benzene, it is clear that the maximum temperature attainable in this apparatus was limited by the removal of heat as latent heat of vaporization of benzene. This experiment shows that the supposed fractional distillation of intensively dried benzene into its pseudo-components can be observed with ordinary undried benzene in a similar apparatus and it is concluded that what Smits and Baker observed was not a separation of benzene molecules in the supposed different states of association, but that they simply noted the phenomena associated with the superheating of benzene.

A phenomenon was observed in the above experiment which was also noted by Baker (1922) in boiling dry benzene, and which he interprets as evidence for different molecular species in the liquid and vapor phases. In boiling dry benzene, Baker noticed that a drop falling from the thermometer in the vapor on the surface of the hot liquid formed a globule 12 mm. in diameter and 5 mm. deep which persisted for more than a minute. He noticed no increase in pressure or other disturbance when the drop coalesced with the rest of the liquid. In one instance in the experiment described above a drop falling from the thermometer remained on the surface of the benzene for ten minutes and increased in size with time. This drop was 7 mm. in diameter when it coalesced. A second drop swam on the surface for five minutes before coalescing. The stability of these drops is undoubtedly caused by a difference in surface tension between the hot liquid and the drop formed in the cooler vapor which gives it a temporary stability, and is not due to any real difference in the state of benzene molecules in the vapor and in the liquid.

Using the apparatus for the experiments with benzene, the superheating of carbon tetrachloride and of water was studied. It was found that carbon tetrachloride could be easily superheated as much as 30°, and that water could be superheated 12°. When boiling did begin, it was not always violent, but was sometimes quiet and regular. There did not appear to be an upper limit to the superheating; the amount of superheating depending on the rate of heating, the cleaning of the apparatus, and absence of motes or foreign particles from the liquid. Water was relatively difficult to superheat but the organic liquids investigated were superheated with ease.

A second condition which obtained in Baker's boiling point measurements and which is favorable to superheating is the use of a heating bath. When heat is supplied by an electrically heated wire in the liquid, superheating is effectively prevented. It has been shown elsewhere[1] that the boiling points of intensively dried liquids show no anomaly when heating is carried out in this way.

A third factor which is favorable to superheating is the removal of nuclei in the liquid which act as centers to start bubble formation. Allowing a liquid to stand with a flocculent solid, such as phosphorus pentoxide, and distillation of the liquid tend to free the liquid of foreign particles.[2]

A sample of dust free benzene was prepared by distilling benzene under high vacuum in a double arm tube using Martin's technique.[3] This benzene examined in the cardioid ultramicroscope by the writer in collaboration with Dr. E. O. Kraemer showed the benzene to be practically dust free. The benzene boiled at 106° when heated in a Nujol bath with a thermometer immersed in the liquid.

Some if not all of the conditions favorable to superheating outlined above obtained in the boiling point measurements described by Baker (1922). Baker's criterion of boiling is the formation of bubbles in the heated liquid. This is not a true criterion of boiling points, as a boiling point is the temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure. The formation of bubbles in a heated liquid is conditioned not only

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[1] Lenher and Daniels: Proc. Nat. Acad. Sci., **14**, 606 (1928).

[2] Spring: Rec. Trav. chim., **18**, 233 (1899).

[3] Martin: J. Phys. Chem., **24**, 478 (1920).

by the pressure and temperature of the liquid but also by the presence of nuclei in the liquid which act as centers from which bubbles can be evolved. If there are no centers to start formation of bubbles in a liquid at its boiling point there will merely be evaporation from the surface of the liquid and then it will not boil in the sense which Baker means when he speaks of boiling liquids. Until it has been shown that the vapor pressure of dried liquids does not equal atmospheric pressure until a temperature above the normal boiling point is reached it cannot be maintained that the boiling points of dried liquids have been raised.

The writer has shown elsewhere[1] that the apparent rise in boiling point of benzene which had been subjected to an electrical potential is due to superheating.[2] It must be noted in this connection that Baker's (1928) surface tension measurements on benzene subjected to a direct current potential, which unfortunately he does not publish, led him to believe that the molecular weight of the benzene had been increased two to three times that corresponding to the formula C_6H_6. Smits[3] has already pointed out the difficulty in accepting these surface tension measurements in view of the fact that the direct current potential has no measurable effect on the vapor pressure or boiling point of benzene. It seems to the writer that these data throw doubt on the accuracy of the surface tension measurements which Baker (1922) made on his intensively dried liquids. These measurements, which are described as preliminary determinations, indicated that the molecular complexity of the liquids had increased on drying. These surface tension measurements together with some later vapor density determinations are the principal basis for the hypothesis that the degree of association of a liquid is changed on drying. Briscoe, Peel and Robinson[4] have recently measured with great care the density and surface tension of intensively dried benzene and find no change which would justify an assumption of a change in degree of association on drying. The writer has recently measured the boiling point and vapor density of intensively dried carbon tetrachloride[5] and has found no change which could be attributed to drying.

Summary

It has been shown that ordinary benzene, carbon tetrachloride, and water can be superheated as much as 30° above the normal boiling point in reproductions of apparatus used in intensive drying work.

The conditions favoring superheating of liquids are discussed.

Objections are raised to the hypothesis that the degree of association of a liquid is changed on prolonged drying.

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[1] Lenher: Nature, **123**, 907, (1929).

[2] Since this paper was written the author has seen the paper by J. W. Smith: J. Chem. Soc., **1929**, 788, in which Smith's experiments lead to the same conclusion.

[3] Smits: J. Chem Soc. **1928**, 2407.

[4] Briscoe, Peel and Robinson: J. Chem. Soc., **1929**, 368.

[5] Lenher, J. Am. Chem. Soc., to be published in October, 1929.

Wilmington, Delaware.

9C-159

STUDIES IN PHOTOGRAPHY*

II. The Rôle of Sensitizers in Photography and the Latent Image

BY FRANK E. E. GERMANN AND DZU-KUN SHEN

The Behavior of Sensitized Silver Iodide Plates. In a recent article Germann and Shen[1] have shown that the silver iodide grains of a photographic plate made of a silver iodide-gelatin emulsion have the same sensitivity irrespective of size. This was demonstrated by making plates from the large and small grains respectively of a centrifuged emulsion. It was also shown that the maximum per cent. of grains which were developable in any case was of the order of 17%. With longer exposure, the period of reversal was entered. Emulsions were of such a dilution as to give one grain layer on the photographic plate.

When one of these plates consisting of grains which were only 17% developable, was bathed in a one per cent. solution of either hydroquinone or pyrogallol, prior to exposure, it was found that the number of developable grains increased with time of bathing until 100% was reached. Prolonged bathing in the sensitizer produced no further effect. The sensitized plate, after being thoroughly washed in running water, does not resume its initial state of low percentage developability, a fact confirming Lüppo-Cramer's early observations.[2] Metol, glycin, and amidol were also tried as sensitizers, and were found to act the same as metol and hydroquinone. Fig. 3 is a composite of many curves and shows their interrelationship better than would be possible with single ones. In cases where the same curve has various numbers, not all points are given, as there would be too much overlapping. With the scale used, practically all of the points fall on the curves, and the various curves represented by one are identical. Thus Plates I, II, and III, which are reproduced from the experiments of our first paper, all yield identical curves, giving a maximum developability of about 17%. Plates IV and V were sensitized for ten minutes with 1% hydroquinone and pyrogallol respectively, and dried without washing. The points at 4096, and 8192 seconds showing reversal, belong only to IV, the maximum time of 2048 seconds having been adopted for all other experiments. Plates VI and VII were sensitized for ten minutes in 1% pyrogallol, the one being dried and then washed in running water for two hours and again dried, the other having been washed for two hours immediately after sensitizing and then dried.

In order to find the relative effect of sensitizers on large and small grains, Plates VIII and IX were prepared. Plate VIII consisted of the large-grain fraction prepared by centrifuging the emulsion as previously described, and Plate IX the small-grained fraction. Both were sensitized with a 1% pyro-

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* Contribution from the Department of Chemistry of the University of Colorado.

[1] Germann and Shen: J. Phys. Chem., 33, 864 (1929).

[2] Lüppo-Cramer: Phot. Korrespondenz, 38, 158 (1901); 40, 25 (1903).

gallol solution for ten minutes, and dried without washing. Thus Plate II before sensitizing corresponds to VIII after sensitizing, and similarly Plate III corresponds to Plate IX.

The power of sensitizing silver iodide plates is not limited to the usual developers, as is shown by Plates X to XV inclusive. Plates X and XI were sensitized for ten minutes with 0.2 and 0.5 per cent. solutions of acetone semicarbazone respectively, and dried without washing. Plates XII and XIII were sensitized for ten minutes with 1 and 5 per cent. solutions of sodium nitrite respectively, and dried without washing. Plate XIV was sensitized for ten minutes in a 1 per cent. solution of sodium sulphite and dried without washing. Sodium nitrite and sodium sulphite, although much stronger halogen absorbers than the usual developers are not such good sensitizers. Plate XV was sensitized for ten minutes with a 1 per cent. solution of sodium bisulphite and dried without washing. It is seen to be as effective a sensitizer as are the usual developers.

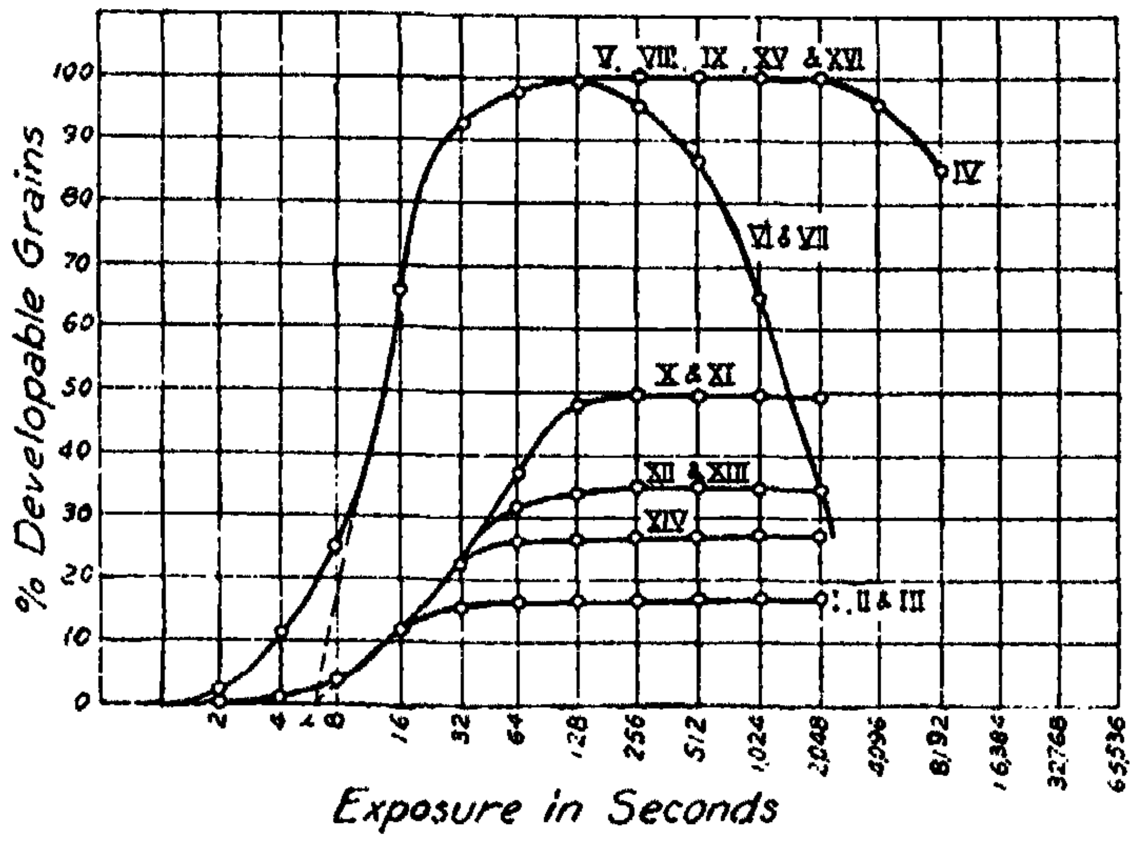

Fig. 3

Sensitivity and Speed. The curves in Fig. 3 are similar to the characteristic curves for the various emulsions, since the percentage of developable grains is proportional to the density of the plate. When the middle, or straight line portions of these curves, which represent the range of correct exposure, are projected until they cut the exposure axis, it is seen that they intersect at a common point marked (i). This point has been called the inertia of the emulsion by Hurter and Driffield, and may be taken as a measure of the speed. Obviously, the greater the inertia the less the speed of the emulsion. Since all these curves intersect at one point, it is obvious that the sensitizers have had no effect on the *speed*, but have merely increased the developability of the grains. Sensitivity is measured in terms of the amount of light that will make the grain developable. A change in sensitivity involves, therefore, a vertical displacement of the curve without changing the value of the inertia (i), while a change in speed involves a horizontal shift in (i). By sensitivity of a grain we mean that the grain is developable if a sufficient exposure is given. Speed represents the degree of sensitiveness. Obviously we can not state that all the grains of a given emulsion have the same speed, but the average of all speeds is proportional to the reciprocal of the inertia.

The terms sensitizers and desensitizers should, therefore, be assigned to those substances which increase or decrease the developability of the grains. Substances which increase or decrease the speed should be called accelerators and retarders respectively.

The Rôle of Sensitizers. Assuming that in a given emulsion we have a wide range of speeds of the various grains, it is obvious that the grains possessing the highest speeds would be developable after a very short exposure. If the exposure is prolonged, then we enter the period of reversal for the fast grains, while at the same time making some of the slower grains developable. A wide range of speeds would accordingly yield a plate of low maximum percentage developable grains. If something can be added to such an emulsion which will prevent the reversal of those grains which have become developable, without interfering with those which have not become developable, then it should be theoretically possible to make all the grains in an emulsion developable if given a long enough exposure. This apparently is actually what happens when a sensitizer is added. When the sensitizer is not washed off, but allowed to dry in excess on the plate, the percentage number of developable grains increases to 100% in some cases, and remains at that value for a considerable overexposure. Finally, when the exposure is very long, the sensitizer seems to be exhausted, and the period of reversal is entered. When excess sensitizer is washed off, reversal comes quickly. The rôle of a sensitizer thus appears to be that of preventing or delaying reversal. If, therefore, sensitivity is merely a case of inhibited reversal, it is very possible that many substances which are at present regarded as insensitive to light may be made sensitive when suitable substances are found to prevent their rapid reversal.

The insensitivity of pure silver iodide emulsions is probably due to the existence of a wide range of speeds among the grains, combined with the phenomena of quick reversal. There might not be any inherent difference in sensitivity between grains, but we must admit that grains in a given emulsion possess different speeds. The constancy of the percentage number of developable grains in the normal unsensitized silver iodide emulsion throughout a wide range of exposures may be explained by assuming that by a given exposure those which have higher speeds may be reversed, while others are just made developable. Equilibrium may finally be reached when the number reversed per unit of exposure equals the number made developable and the horizontal portion of the curve results. If a certain critical amount of light energy is required to make a grain developable, and a definite small increment of that amount would make it reverse, the curve of the reversal should exactly repeat the curve of developability, but in a reverse direction. This is most probably the case as indicated by Curve No. VI and VII, Fig. 3. This simply means that the course of reversal follows exactly the rule that governs the developability of the grains.

Indeed it is not definitely known that the photographic effect is an instantaneous one on account of the intermittency effect of the photographic plate; conversely we have no right to assume that reversal is instantaneous. Since the phenomenon of reversal actually takes part even in a normal exposure[1] of a modern fast plate, it becomes evident that such a phenomenon cannot be neglected in the study of photographic processes. The failure of the reciprocity law seems very likely to be due, among other factors, to the intervention of reversal.

Solarization or Reversal. Numerous theories have been offered to explain the phenomenon of reversal, the question still remains unsettled. If the action of light is to affect the grains in such a way as to initiate development, it is rather difficult to see how excessive exposure could destroy the effect already produced. The solarization can not be the reversed reaction of that producing the latent image, because reversible reactions would come to an equilibrium as their ultimate stage. It is thermodynamically impossible that a reaction goes to completion in one direction and then completely reverses to its original state under the same external conditions. The view that the chemical composition of the solarized image is different from that of the normal latent image and that the silver halide grains having received a solarizing exposure are chemically different from the normal unexposed grains, is a very debatable assumption. Arguments of this nature will ultimately lead to the ever-present controversy over the chemical or physical nature of the latent image. In fact, we have proven experimentally that solarized grains are practically identical to the normal unexposed grains in the case of silver iodide emulsions so far as their behavior towards sensitizers is concerned. When a silver iodide one-grain layer plate which has been exposed to complete solarization is sensitized with a 1% pyrogallol solution, the exposure-developability curve falls exactly on that of the similarily sensitized normal plate. This is shown by Plate XVI of Fig. 3 which was a one-layer silver iodide emulsion exposed twenty minutes to a 150 Watt incandescent lamp at a distance of ½ meter, then sensitized with a 1% pyrogallol solution for ten minutes, and dried without washing.

Photo-Retrogression. Another interesting characteristic of the silver iodide plate is its rapid photo-retrogression. On one occasion, a silver iodide plate was exposed and left undeveloped for twelve hours. On developing, the maximum percentage developable grains was reduced to half of what it would have been had the plate been developed immediately after exposure. The nature of photo-retrogression, though very little understood, is probably due to the same causes as reversal.

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[1] Svedberg: Phot. J., 64, 272 (1924).

Action of Oxidizing Agents on Sensitivity and Speed. The speed of a very fast plate may be reduced by washing in a solution of chromic acid. The latter is considered to be a solvent for the sensitivity material.[1] It is not only a good oxidizing agent, but is also an excellent solvent for silver. The silver iodide emulsion was found to have considerable resistance towards the action of chromic acid. Both the speed and sensitivity of a normal unsensitized silver iodide plate undergo very little change when bathed in chromic acid for a short time with or without pre-exposure. The action does not begin to be appreciable until the plate has been bathed for three hours, and it becomes a maximum after bathing fifteen hours. The action on large and small grains is identical.

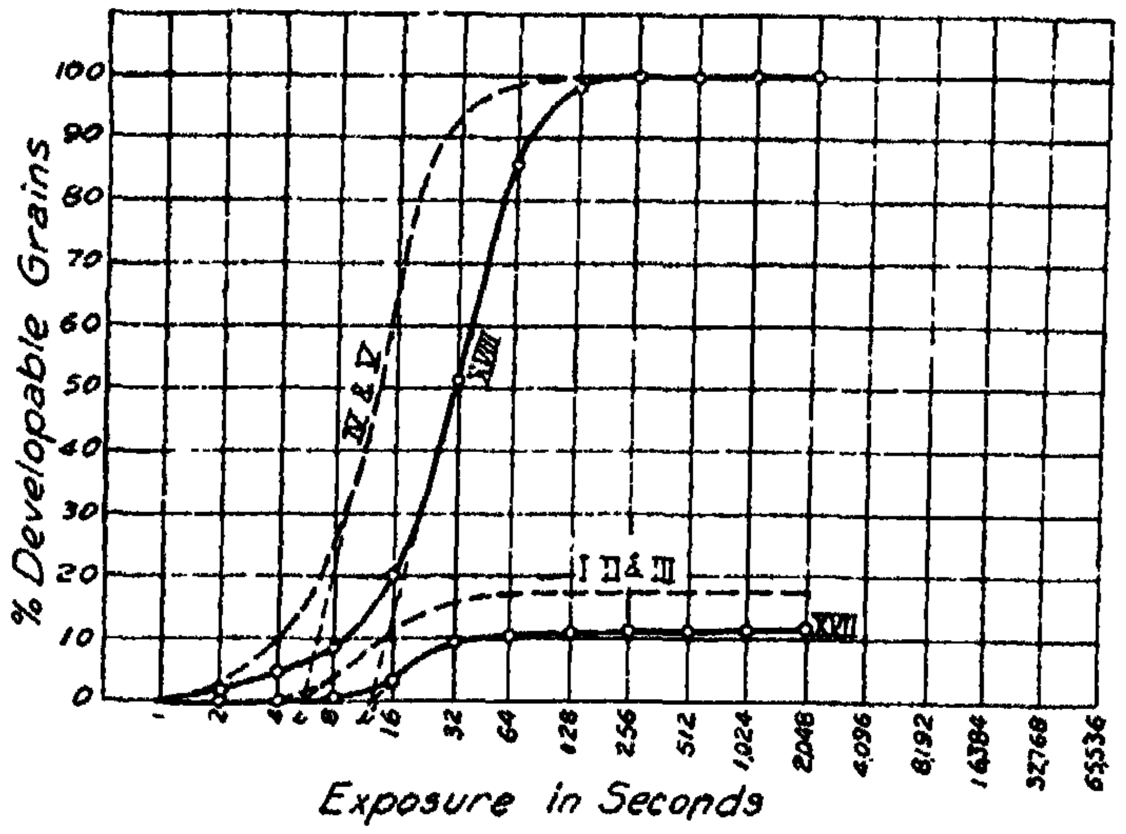

Fig. 4

In Fig. 4, Plates I, II, and III we have reproduced the curve for normal unsensitized silver iodide plates. We have also given the curve for Plates IV and V which had been sensitized. The curve for Plate XVII was produced by taking the normal unsensitized silver iodide plate and bathing it in a solution containing 0.5% CrO_3 and 0.2% H_2SO_4 for fifteen hours, followed by washing for three hours in running water and then drying. The curve for Plate XVIII resulted when a plate like the above had been bathed for the same length of time in the same solutions, washed for three hours, dried, and then sensitized with a 1% pyrogallol solution for ten minutes. It was finally dried without washing. The projected normal exposure curves show that bathing in chromic acid shifted the inertia value from (i) to (i′), thus reducing the speed. Here again we see that the sensitizer increases the developability, but does not bring the speed back to the original value.

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[1] Clark: Phot. J., 63, 230 (1923); 64, 91 (1924); Trans. Faraday Soc., 19, 309 (1923); Sheppard: J. Franklin Inst., 198, 507 (1924).

The Mechanism of Latent Image Formation. Trivelli,[1] in a recent paper, proposes a theory correlating the photo-electric property and the formation of the latent image. It is assumed that when light falls on the silver halide grain containing specks of silver sulphide or silver, the greater photo-electric effect of silver sulphide or silver compared with that of silver bromide produces a difference in potential and that the photo-conductivity produced by the action of light causes an electrolytic deposition of silver in the neighborhood of the speck. This increases the size, and in consequence the developability of the grain. If the sensitivity speck consists of silver sulphide and silver, an elementary photo-electric circuit is possible, silver being the cathode, silver sulphide the anode and silver bromide the solid electrolyte, thus in this cell:

$$\overset{-}{\mathrm{Ag}} \quad \Big| \quad \underset{\xleftarrow{\hspace{8em}}}{\mathrm{AgBr}} \quad \Big| \quad \overset{\quad +}{\mathrm{Ag_2S^+}}$$

the elementary electric current runs through the silver bromide towards the silver cathode, hence the silver cations from the silver bromide move towards the silver cathode. The silver speck, therefore, increases in size until developability is reached.

This theory is plausible in itself. Unfortunately, a process of this type cannot explain the phenomenon of reversal produced by the prolonged exposure to the action of light, unless some additional assumptions are made. During the photo-electrolysis, silver cations move towards the silver cathode, building up a nucleus large enough to initiate development; simultaneously bromine anions move towards the silver sulphide anode where a secondary compound might be formed. Accordingly, the silver sulphide speck merely acts as a bromine acceptor, a theory originally proposed by Hickman.[2] The accumulation of bromine, which may either cause partial or complete polarization of the cell or form a compound with the silver sulphide having a lower potential in comparison with that of silver, would only result in a state of equilibrium, and not a cell having its current flowing in an opposite direction so as to bring the system to its original condition.

In order to overcome this, we might, however, assume that the substance acting as an anode in such a photo-electrolysis is not pure silver sulphide but a substance which is photo-sensitive itself and undergoes continuous decomposition by the action of light with the production of a less photo-sensitive substance having a lower potential in comparison with that of silver, then during the exposure to the action of light, two simultaneous processes take place according to the following scheme:

$$\begin{array}{cccccc} & & \multicolumn{3}{c}{\xrightarrow{\hspace{8em}}} & \\ (1) & \mathrm{A} & \Big| & \mathrm{AgBr} & \Big| & \mathrm{Ag} \\ & \downarrow & & & & \\ (2) & \mathrm{B} & \Big| & \mathrm{AgBr} & \Big| & \mathrm{Ag} \\ & & \multicolumn{3}{c}{\xleftarrow{\hspace{8em}}} & \end{array}$$

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[1] Trivelli: J. Franklin Inst., 204, 649; 205, 111 (1927).

[2] Hickman: Phot. J., 67, 34 (1927).

where A represents the original sensitivity speck and B its photo-decomposition product having a lower potential than that of silver. During the exposure, the rate of electrolysis in the cell (1) will at first gradually fall until a point is reached at which we have a state of equilibrium corresponding to a complete polarisation of the cell. Since the transformation of A into B is independent of the cell (1), this transformation will proceed as long as the light is acting upon it until all of A is destroyed and the resulting reversed cell (2) will work at its full capacity. A complete reversal results.

Now, in the case of silver iodide plates, the sensitizer may be considered as an iodine acceptor in accordance with the above point of view. It is not a halogen absorber in the sense of a chemical reaction because stronger halogen absorbers such as sodium nitrite, etc., do not act in the same way. Without the presence of the sensitizer, the photo-electrolysis cannot take place, and hence undevelopability of the grains. The speed of the grain, however, depends on the original size of the silver speck upon which more silver can be deposited through the process of photo-electrolysis. The greater the original size of the silver specks the less the light energy required to build up a nucleus large enough to initiate development. The size of the silver specks in the grains is solely determined at the time the emulsion is made and cannot be altered by any means of sensitizing. This explains the fact that sensitizers only affect the developability but not the speed of the grains.

The fact that a silver iodide plate which has been bathed in a solution of the sensitizer could not be brought back to its original condition by prolonged washing in running water seems to indicate that chemical combination takes place between the sensitizer and the silver iodide or something therein. Before we have definite proof of any chemical compound being formed, the retaining of a small amount of the sensitizer by the silver iodide crystal may be assumed to be a case of adsorption in the sense of Langmuir's molecular layer.[1] Whether the molecular complex that is formed between the sensitizer and silver iodide itself or the chemical compound between the sensitizer and something else contained in the silver iodide crystal is operative during the process, is a question we are not yet able to answer with absolute certainty. Since development starts at points even in the unwashed sensitized grains, it appears probable that only these points in the grains are susceptible to the action of sensitizing. The original points in the silver iodide grains may be of such a nature that they are unable to function as sensitive specks until a new complex is formed with the sensitizer. The size of the sensitive specks thus formed will depend upon the amount of the sensitizer actually in contact with them in one or more molecular layers. During washing of the sensitized plate, the outer layers of the sensitizing material can be washed off easily, while that layer formed at their molecular interface, being held by the force of the secondary chemical valence of the crystalline surface, can be removed only with difficulty.

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[1] Langmuir: J. Am. Chem. Soc., **37**, 1163 (1915); **38**, 2221 (1916); **39**, 1848 (1927); Trans. Faraday Soc., **17**, 607 (1922).

In the case of the unwashed sensitized plates, the presence of an excessive amount of the sensitizer tends to prevent the occurrence of reversal to an extent proportional to the amount of the sensitizer attached on the surface of the grain, that is, the more the amount of the sensitizer present, the later the reversal takes place. This can only be explained by assuming that the amount of the sensitizer is continuously changing during the exposure: It appears probable that the sensitive layer undergoes successive destruction by the action of light outwards from their molecular interface; in other words, fresh sensitizing specks are continuously formed at the expense of the sensitizing material present until all of the sensitizing material is destroyed and the reversal takes place. In this way, the length of the horizontal portion of the curve representing complete developability of the grains is seen to be dependent on the number of molecular layers of the sensitizing material situated upon the sensitive specks. Furthermore, with this theory, it is not difficult to explain the fact that solarized plates can be sensitized, after which they behave exactly as the normal unexposed plates.

Various attempts made to increase the sensitivity or speed of the silver iodide emulsion by ripening or by varying the proportion of reagents used in making the emulsion seemed to be unsuccessful. The emulsion made with an excess of silver nitrate fogged very badly by chemical development without any appreciable increase in speed. An emulsion containing neither excess of silver nitrate nor potassium iodide has little difference in photographic properties from the one formed with an excess of potassium iodide, gives grains of larger sizes and contains fewer clumps. The low speed of the silver iodide emulsion appears probably to be due to the reluctance of the silver iodide to be reduced by the organic compounds present in gelatin; hence there is little increase in the size of silver specks in the process of ripening.

The Spectral Sensitivity of Silver Iodide Emulsions. The question naturally arises whether the action of the sensitizers on the silver iodide plates effects any change in spectral sensitivity of the silver iodide. The sensitizers used are in general reducing agents and some are active developers. It may be argued that the increase in sensitivity may be due to silver nuclei produced by the action of the reducing agents upon the silver iodide grains. This was, however, proved not to be the case, since the sensitivity of the sensitized plates could be reduced to some extent by washing with alcohol before exposing. This we know does not dissolve metallic silver. The fact that the spectral sensitivity of the sensitized plates is identical with that of the normal plate seems conclusive proof that silver nuclei are not produced by sensitizing, because colloidal silver is known to act as a panchromatic sensitizer of photographic plates.[1]

Spectrographs No. 1 to 5 were made by exposing the multi-layer silver iodide plates to a carbon arc spectrum in a Hilger quartz spectrograph and developed in pyro-soda developer, followed by fixing in an acid fixing bath.

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[1] Lüppo-Cramer: Phot. Ind., **18**, 37 (1920); **22**, 982 (1924); Fajans and Frankenburger: Z. physik. Chem., **105**, 255, 329 (1923); Z. Elektrochemie, **28**, 499 (1922).

The emulsion was made in the same manner as that for the single layer plates. After being washed it was coated on glass plates without further addition of water.

Spectrograph No. 1 Silver iodide normal plate.

Spectrograph No. 2 Silver iodide plate sensitized with 1% pyrogallol solution for ten minutes, dried without washing.

Spectrograph No. 3 Silver iodide plate sensitized with 1% hydroquinone solution for ten minutes, dried without washing.

Spectrograph No. 4 Silver iodide plate sensitized with a solution containing 1% pyrogallol and 1% sodium carbonate for ten minutes, dried without washing.

Spectrograph No. 5 Silver iodide plate sensitized with 1% sodium bisulphite solution for ten minutes, washed for one hour in running water and dried.

These plates, which are not reproduced here, all have practically the identical spectral sensitivity as the pure silver iodide plate, in the region 300-460 $\mu\mu$. Alkali does not affect the spectral sensitivity as shown by Spectrograph No. 4. The theory of Fajans[1] of the hydroxide-body, apparently does not apply in this particular case. The panchromatizing effect of sodium bisulphite found by Capstaff[2] is not operative in the case of a pure silver iodide emulsion as shown by Spectrograph No. 5. It is generally known that the speed of an emulsion depends on the alkalinity. Here, sodium bisulphite is an active sensitizer,[3] while sodium sulphite is inactive.

The antagonistic action of light of different wave lengths has been called the Herschel effect. It might be argued that the insensitivity of silver iodide plates is due to this effect. This assumption was tested and proved to be false by exposing a plate under a light filter (Corning glass G985B) transmitting light of wave lengths from 240 to 480$\mu\mu$. The developability-exposure curve was similar to those of the plates exposed to white light. This leads one to the conclusion that the latent image can be destroyed by light of the same wave length as that producing it. In agreement with this Renwick[4] found that the reversing rays were restricted to the region 430 to 480$\mu\mu$ for silver iodide emulsions.

Summary

(1) It is shown that by the use of chemical sensitizers more of the grains of a silver iodide emulsion may be made developable *in certain cases*. Pyrogallol, hydroquinone, metol, amidol, glycin, and sodium bisulphite effect 100% developability, while sodium nitrite, sodium sulphite, and acetone semicarbazone are less effective.

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[1] Fajans and Frankenburger: Z. physik. Chem., **105**, 255, 329 (1923); Z. Elektrochemie, **28**, 499 (1922); Fajans and Steiner: Z. physik. Chem., **125**, 307 (1927); Lüppo-Cramer: Phot. Ind., **22**, 357 (1924).

[2] Capstaff: Brit. J. Phot., **67**, 719 (1920); J. Franklin Inst., **190**, 87 (1920); "Silver Bromide Grain," Monograph, p. 53 (1921).

[3] Rawling: Phot. J., **66**, 495 (1926); **67**, 42 (1927).

[4] Renwick: J. Soc. Chem. Ind., **39**, 156T (1920).

(2) The use of the terms sensitivity and speed is discussed and the terms sensitizers and desensitizers are suggested for those substances which increase or decrease developability. Similarly the terms accelerators and retarders are suggested for those substances which increase or decrease speed.

(3) The rôle played by sensitizers is discussed and rather conclusive experiments are given to show that the action is merely one of preventing or retarding reversal.

(4) It has been proved that solarized grains are practically identical to unexposed grains in the case of silver iodide emulsions. A completely solarized plate can be sensitized with one of the various sensitizers used, and its exposure-developability curve coincides with that of a sensitized plate which has not been solarized.

(5) The effect of chromic acid on normal silver iodide plates is studied, and it is found that both the speed and sensitivity is reduced. Resensitizing such a plate restores the sensitivity, but does not restore the speed, thus showing again that the action of sensitizers is that of increasing developability only.

(6) Trivelli's hypothesis of the latent image is modified in order to correlate the phenomenon of reversal with the mechanism of latent image formation. It is assumed that the sensitive specks consist of silver germs and a molecular complex of the sensitizer which function as an iodine acceptor during exposure. It is the presence of this sensitive complex in the grain that makes the development of the exposed grains possible. The speed of the grains, however, depends on the size of the silver germs which are formed at the time the emulsion is made and can not be altered by any method of sensitizing. The sensitizing complex is assumed to undergo a continuous decomposition by the action of light, and thus causes the phenomenon of reversal to take place when the sensitivity material is completely destroyed.

(7) The sensitizers are not optical sensitizers. The spectral sensitivity of the sensitized plate is identical with that of the normal silver iodide plate.

(8) It is shown that the insensitivity of silver iodide emulsions is not due to the antagonistic action of light of different wave lengths, known as the Herschel effect.

INDUCED REACTIONS

BY WESLEY G. VANNOY

Mellor[1] and Friend[2] both include in their text-books good discussions of the early work on induced reactions. In general, F. Mohr[3] has received credit as being the first to notice such a phenomenon. He noted, over a century ago, that an aqueous solution of sodium arsenite did not undergo any perceptible change when shaken with air, while a solution of sodium sulphite was oxidized rapidly under the same conditions. Further, he found that when a mixture of sodium sulphite and sodium arsenite was treated in this manner both salts were oxidized. Various names have been used to designate this type of reaction, such as chemical induction, auto-oxidation, sympathetic, coupled, and induced reactions. Kessler[4] appears to have been the first to study the subject systematically and he introduced the term, induced reactions, and the other nomenclature which is used most commonly at the present time. He called the fastest reaction the primary reaction; the induced reaction caused by or helped along by the change the secondary reaction; the substance which takes part in both reactions the actor; the substance which takes part in the primary reaction the inductor; and the substance which takes part in the secondary reaction the acceptor. He found many examples of induced reactions but made no attempt to explain them. Since his time, numerous theories have been suggested to explain the nature of these reactions. The most important of these will be mentioned briefly in this article.

Manchot's Peroxide Theory[5]:—In every process of oxidation there is formed a primary oxide which has, in general, the characteristics of a peroxide. The peroxide is formed directly from the reagents, and intermediate states are passed over.

$$2FeO + nO_2 = Fe_2O_{2n+2} = Fe_2O_3 + (2n - 1)O$$

He believed that the formula could be deduced from a determination of the induction factor, which is the proportion in which the actor divides itself between the inductor and the acceptor.

$$\text{Induction Factor} = \frac{\text{Amount of acceptor oxidized}}{\text{Amount of inductor oxidized}}$$

Luther and Schilow's Classification[6]:—They believe that information on the nature of the intermediate compound formed can be obtained by suit-

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[1] Mellor: "Chemical Statics and Dynamics," 333.

[2] Friend: "Textbook of Inorganic Chemistry," 7 I, 55.

[3] Mohr: "Lehrbuch der chemischen-analytischen Titriermethoden," 271 (1855).

[4] Pogg. Ann., **95**, 216 (1855); **119**, 218 (1863).

[5] Manchot: Ann., **325**, 93, 105 (1902).

[6] Luther and Schilow: Z. physik. Chem., **46**, 777 (1903).

able variation of the reagents. "Observations of the occurrence or non-occurrence of induction when the reagents are varied systematically enables one, therefore, to a certain extent to decide which of the substances play a specific rôle in the reaction." The nature of the classification is as follows: Class A, the inductor is 'specific' and the actor and acceptor are 'non-specific.' Classes B and C, the actor and the acceptor take the place respectively of the inductor in Class A. Class D, both the acceptor and the inductor are 'specific,' and the intermediate body must be regarded as a complex derived from both of them. Classes E and F, the inductor and the actor, or the acceptor and the actor are 'specific' respectively.

Miller's Classification[1].—He prepared a classification based on kinetic measurements. According to this, the induced reactions are divided into three classes.

Class 1. Cases of catalysis combined with the destruction of the catalyzer.

Class 2. Cases in which the reaction between the actor and the inductor is the same whether the acceptor be present or not. The peroxide theory would come under this heading.

Class 3. Cases in which the reaction between the actor and the inductor changes when the acceptor is present.

This classification of course involves kinetic measurements and the comparing of the rates at which the actor reacts with the inductor and acceptor separately and combined.

In addition to these three classifications, a number of hypotheses have been advanced to explain the particular reaction or group of reactions studied. Schönbein[2] in 1858 attempted to explain the formation of hydrogen peroxide or of ozone, when many different substances were exposed to atmospheric oxidation on Brodie's assumption[3] that the oxygen molecule consists of a positive atom united to a negative atom. Under these conditions he argued that the metal would unite with the negative atom and the water with the positive atom. However, he could not substantiate this view with any experimental evidence and, as a consequence, it has not been generally accepted. Hoppe-Seyler[4] suggested the formation of nascent oxygen during the oxidation of a substance, which then united with water to give hydrogen peroxide. Traube[5] would not accept Hoppe-Seyler's explanation and expressed the view that, since water was essential for the oxidation, the oxygen used by the substance undergoing oxidation came from the water. The hydrogen thus liberated would react with molecular oxygen giving hydrogen peroxide. This theory was modified somewhat by Bach[6] and by Engler and Wild,[7] who held that the oxygen molecule could combine as a whole with sub-

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[1] Miller: J. Phys. Chem., 11, 91 (1907).

[2] Schönbein: J. prakt. Chem., 75, 99 (1858).

[3] Brodie: J. Chem. Soc., 4, 194 (1852); 7, 305 (1855).

[4] Hoppe-Seyler: Z. physiol. Chem., 2, 222 (1881); Ber., 16, 117 (1883).

[5] Hoppe-Seyler: Z. physiol. Chem., 2, 222 (1881); Ber., 16, 117 (1883).

[6] Bach: Compt. rend., 124, 951 (1897).

[7] Engler and Wild: Ber., 30, 1669 (1897).

stances other than hydrogen, giving rise to higher peroxides of the inductor which then react with the acceptor. Schilow[1] made use of stable and instable intermediate compounds to explain the mechanism of the reactions which he studied. Miss Benson[2] developed what she called a "Ferro-iod-ion Theory," assuming the formation of an intermediate compound to explain the mechanism of the reaction, chromic acid, ferrous sulphate, and potassium iodide. Winther[3] suggested short-wave radiation as an explanation of reactions of this kind.

Each of the above hypotheses may apply to a limited number of induced reactions; but it is rather difficult to be sure just where any particular one may apply. Manchot's peroxide theory apparently does not hold for all induced reactions, according to results as shown by Miss Benson, and further, it seems that the peroxide which he postulates must vary in composition, without any reason being given, in order to account for the reactions which he studied. The classifications by Miller, as well as those by Luther and Schilow, are general and could perhaps be applied to all induced reactions. In many cases, however, the application would be somewhat tedious and, even after the classification, the true mechanism of the reaction would still be in doubt.

With these facts in mind, Professor Bancroft[4] has developed and introduced the following theory of induced reactions. Let A be an oxidizing agent (actor) which will not react or which reacts very slowly with a reducing agent C (acceptor); but which reacts with a reducing agent B (inductor) and with C in presence of B. The ratio of C oxidized by A to B oxidized by A is called the reduction factor.

Case 1. B may catalyze the reaction between A and C. If so, the induction factor will increase indefinitely with the relative increase of C in case one adds A to a mixture of B and C. The induction factor will approximate zero in case one adds B to a mixture of A and C so slowly that B is used up practically instantaneously. B will be specific and we cannot substitute another reducing agent for it. Electrolysis will not necessarily accelerate the reaction between A and C.

Case 2. C may react with a lower stage of A. Thus $HBrO_3 \longrightarrow HBrO_2$ which reacts with C. Slow addition of B to a mixture of A and C should give approximately two for an induction factor with bromic acid as A. Addition of bromic acid to a mixture of B and C will give an induction factor of approximately zero when B is in large excess, and a value of two when C is in large excess. With different B's the induction factor will vary for any given concentration of B and C. A is specific; but B may be any suitable reducing agent.

Case 3a. C may react with a stable oxidation product of B. So long as there is an excess of C, B will remain apparently unchanged and the induction

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[1] Schilow: Z. physik. Chem., **42**, 641 (1903).

[2] Benson: J. Phys. Chem., **7**, 356 (1903).

[3] Winther: Z. physik. Chem., **100**, 566 (1922).

[4] Bancroft: J. Phys. Chem., **33**, 1184 (1929).

factor will be infinite. With an excess of A the induction factor will be determined by the actual ratio of C to A. A case of this kind is A = O_2, B = HI, and C = SO_2. This is what has been called a consecutive reaction.

Case 3b. C may react with a higher instable stage of B. Thus $Fe^{II} \longrightarrow Fe^{VI}$ which reacts with C. If B is added slowly to a mixture of A and C, the limiting induction factor should be obtained. If B is added to A alone, it should be possible to get more reduction of A than corresponds, for instance with the formation of stable Fe^{III} (evolution of oxygen). B is specific; A may be any suitable oxidizing agent. One might perhaps substitute but a suitable anode for A.

Case 4. B and C form a complex (hydroquinone or aldehyde with sulphite) which reacts with A. If we add A to a mixture of B and C containing so much C that there will be no free B, we shall get a limiting induction factor provided the rate of reaction of A with C is negligible. Addition of B to a mixture of A and C will give approximately zero for the induction factor if the rate of reaction of A with B is high relatively to the rate of formation of the complex of B and C. B and C are specific; but A may be any suitable oxidizing agent. A suitable anode may be substituted for A.

Case 5. Nos. 1-4 may occur simultaneously in any combination. This will usually show itself by positive tests in at least two of the preceding cases. Each problem will then have to be considered on its own merits.

The order of the reaction velocity equation for A and B may be normal for Nos. 1 and 4, whereas it may be abnormal for Nos. 2 and 3, being necessarily abnormal for A in No. 2 and for B in No. 3. With Nos. 1, 2 and 3, the order of the reaction velocity of A and B will be independent of C; but this will not be true of No. 4. The effect of temperature should be studied. The relative stabilities of the various intermediate compounds may vary considerably with changing temperature. One difficulty here will be that at the higher temperatures A may react with C at any annoying rate even in the absence of B.

Experimental Part

Chromic Acid, Arsenious Acid and Tartaric Acid

Among other reactions, Schilow[1] studied the induced oxidation of tartaric acid by chromic acid in the presence of arsenious acid. The reaction was previously observed by Kessler who had verified this induction in the cases where AS_2O_3, $FeSO_4$, $K_4Fe(CN)_6$, Sb_2O_3, SnO, and SO_2 acted as inductors. The results of Schilow's investigation are given in Table I, and Figs. 1a and 1b.

He obtained a maximum induction factor of 2.8 with increasing sodium tartrate concentration and hence with an increasing ratio of tartrate to arsenite concentrations. He further showed that the induction factor was independent of the concentration of the arsenious acid provided the ratio of the concentrations of tartrate and arsenite were kept constant. When he

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[1] Loc. cit.

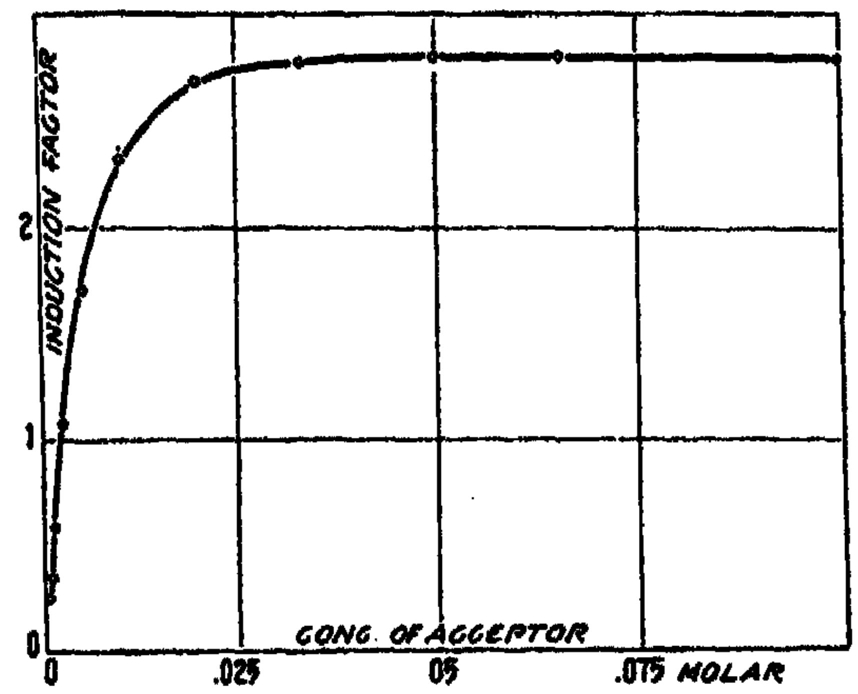

FIG. 1a

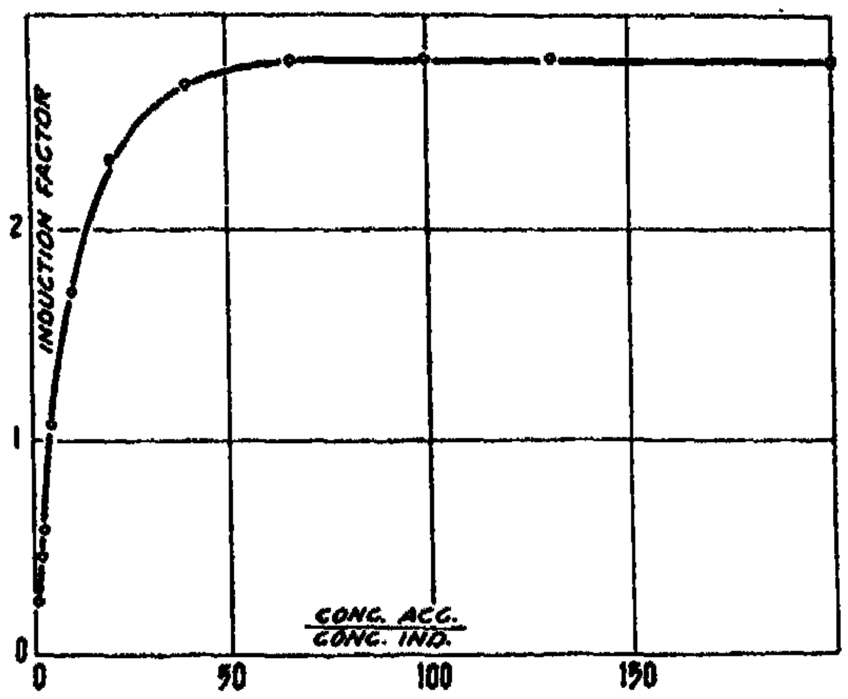

FIG. 1b

TABLE I

Reaction Mixture: 10 cc N/100 $K_2Cr_2O_7$; 10 cc N/10 H_2SO_4; 5 cc N/100 As_2O_3; 5 cc of Acceptor. Titrated with N/200 $Na_2S_2O_3$ and N/200 I_2 Solutions.

Conc. Acc. Molar	Ind. Factor	$\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$	Conc. Acc. Molar	Ind. Factor	$\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$
1/2000	0.25	1(=0.20)	1/200	1.70	10.
1/1600	0.30	1.25	1/150	2.02	13.2
1/1400	0.34	1.43	1/100	2.32	20.
1/1200	0.40	1.65	1/50	2.69	40.
1/1000	0.46	2.	1/30	2.79	66.
1/800	0.58	2.5	1/20	2.80	100.
1/600	0.75	3.3	1/15	2.80	132.
1/400	1.07	5	1/10	1.79	200.
1/300	1.39	6.6			

increased the concentration of the chromic acid the determinations became difficult to carry out due to spontaneous or voluntary oxidation of the tartaric acid.

Considering these results in the light of the above theory it would seem that the nature of this reaction was described by Case 2. Namely, that the tartaric acid (acceptor) must react with a lower stage of chromic acid (actor) since the arsenious acid (inductor) was not specific and could be replaced by various other reducing agents. Under these conditions however with the maximum induction factor of 2.8 as determined by Schilow, the formula for the lower stage of chromic acid would be complex and improbable. (Cr_6O_{11}, etc., depending on just how one postulated the reaction to occur.)

TABLE II

Solutions: N/100 $K_2Cr_2O_7$; N/10 H_2SO_4; N/100 As_2O_3; N/200 $Na_2S_2O_3$; N/200 I_2 and Molar $NaKC_4H_4O_6$ (From which the necessary concentrations for the acceptor were made by dilution). Time given for reaction to take place I-24 hrs. II-96 hrs.
Temp. 22°C (Room).
Control Reactions:

1. 10 cc $K_2Cr_2O_7$ = 20 cc $Na_2S_2O_3$
2. 10 cc $K_2Cr_2O_7$ = 5 cc As_2O_3 = 10 .1 cc $Na_2S_2O_3$
3. 10 cc $Na_2S_2O_3$ = 10 cc I_2
4. 10 cc $K_2Cr_2O_7$ + 5 cc N/10 $NaKC_4H_4O_6$ = 20 cc $Na_2S_2O_3$
5. 10 cc $K_2Cr_2O_7$ + 10 cc H_2SO_4 + 5 cc $NaKC_4H_4O_6$ = I–6.5 cc $Na_2S_2O_3$ II–0 cc $Na_2S_2O_3$

Reaction Mixture: 10 cc $K_2Cr_2O_7$; 10 cc H_2SO_4; 5 cc As_2O_3 and 5 cc Acc. as indicated.

No.	Acc.	Titre I	Titre II	$K_2Cr_2O_7$ used by Acc.	$K_2Cr_2O_7$ used by Ind.	I.F.	I.F. (by Schilow)	Agent
1	M/1200	6.1	5.9	4.1	10	0.41	0.40	$Na_2S_2O_3$
2	M/400	0.2	0.2	10.3	9.8	1.05	1.07	I_2
3	M/100	3.9	3.85	14.	6.1	2.29	2.32	”
4	M/20	4.5	4.6	14.6	5.5	2.8	2.8	”
5	M/10	4.3+	4.2+	14.3	5.7	2.5+	2.8	”
6	Molar			Fading end-point				
7	25 cc Molar							

It was then thought that the reaction might be a combination of Cases 1 and 2 or possibly Case 4 in the above theory, the former however being the most probable. If this were the solution then an increase in the ratio of the concentration of the acceptor to the concentration of the inductor should give rise to a considerable increase in the value of the induction factor. With this in view Schilow's work was repeated and an attempt was made to work at higher concentrations with the acceptor (tartaric acid). His methods were followed throughout. Namely, definite quantities of potassium dichromate, arsenious acid, sodium tartrate and sulphuric acid were mixed and allowed to react at room temperature. After a time sufficient for the reaction to go to completion either the excess arsenious acid was titrated with iodine in an excess sodium bicarbonate solution or the excess chromic acid by means of iodine liberated from potassium iodide in acid solution with sodium thiosulphate. This was done by adding an excess of potassium iodide and 10 cc of 2N sulphuric acid, then after two or three minutes the solution was diluted and titrated as rapidly as possible. This method was shown to be satisfactory by Schilow.

The method used to calculate the amounts of chromic acid used by the acceptor and the inductor was as follows:

1. Excess Chromic Acid, M/1200 Acc.
   Used by Acc. $10.1 - 6 = 4.1$ pts.
   " "Ind. $20.1 - 10.1 = 10$ pts.
2. Excess Arsenious Acid, M/20 Acc.
   Used by Acc. $10.1 + 4.5 = 14.6$ pts.
   " "Ind. $10 - 4.5 = 5.5$ pts.

The data obtained, as seen from Table II, checked Schilow's results in a very satisfactory manner for all concentrations of the acceptor up to the tenth-molar solution. In all cases however where the concentration of the acceptor was tenth-molar or above, checks could not be obtained. Accurate titrations could not be made because of fading end-point. On standing, potassium tartrate was precipitated from the solution. Further it was noted that $K_2Cr_2O_7$ oxidized $NaKC_4H_4O_6$ directly and to a considerable extent in an acid solution as is shown by the fifth control reaction in Table II. These difficulties have been investigated and will be discussed in more detail.

Investigation of Tartrates

The following tartrates were examined with the idea of trying to find one which would not react with chromic acid or one which would react only with the slowest possible rate. 10 cc of a molar solution of the various tartrates were mixed with 10 cc of N/100 $K_2Cr_2O_7$ and 10 cc N/10 H_2SO_4. The time required for the complete reduction of the $K_2Cr_2O_7$ was used as a means of comparison.

No.		Tartrate	Time
1.	Recrystallized	$NaKC_4H_4O_6$ (washed with alcohol)	12 hrs.
2.	Kahlbaum's	$NaKC_4H_4O_6$	12 "
3.	" pwd.	"	6 "
4.	Baker's	"	18–24 "
5.	" recrystallized	" (not washed)	18 "
6.	Kahlbaum's	$H_2C_4H_4O_6$	10 minutes
7.	B and A	$K_2C_4H_4O_6$	19 hrs.
8.	Merck's	"	24 "
9.	B and A	$Na_2C_4H_4O_6$	18 "
10.	Merck's	"	23 "
11.	Prepared	$NaKC_4H_4O_6$	20–23 "

The rochelle salts were made as indicated by the following equations using Merck's potassium tartrate and C.P. sodium carbonate. (Na_2CO_3 for analysis).

$$K_2C_4H_4O_6 + H_2SO_6 \longrightarrow KHC_4H_4O_6 + K_2SO_4$$

$$2KHC_4H_4O_6 + Na_2CO_6 \longrightarrow 2KNaC_4H_4O_6 + H_2CO_3$$

The acid tartrate crystals were washed thoroughly and dried. Calculated amounts were then dissolved in water with sodium carbonate. After the reaction was complete the rochelle salts were crystallized from the solution.

From the tests it was concluded that chromic acid would oxidize slowly any pure tratrate. Further, that Merck's sodium tartrate would serve best in the induced reaction under consideration since its rate of oxidation by chromic acid was lower than that of any other tartrate, with the exception of Merck's potassium tartrate, and its solubility would be sufficient to prevent the precipitation of the acid tartrate in acid molecular solutions of the salt.

Investigation of the Fading End-point

In the foot-notes of his article Schilow made mention of this fading end-point and stated that it was probably due to the reduction of the iodine by the oxidation products of the tartrate. He however made no allowance for this in his iodine titrations.

Since good end-points were obtained in the cases of low tartrate concentrations two methods of obtaining good end-points in the case of high tartrate concentration seemed possible. First, precipitate the tartrate in the form of acid potassium tartrate, filter and titrate the filtrate. Second, after the reaction had come to equilibrium, dilute the desired amount and make the titration. Neither of these two methods however proved to be satisfactory as fading end-points were obtained in both cases.

Solutions of varied composition were then titrated with iodine in an attempt to locate the cause of the fading end-point. The concentration of the solutions used were, molar $Na_2C_4H_4O_6$, for the rest the same as used in the previous experiments.

No.	Solution	cc I_2 Titre	End-point
1.	5 cc As_2O_3	10.2	Does not fade
2.	" + 5 cc $Na_2C_4H_4O_6$ + 10 cc H_2SO_4	10.1	Fades very slowly
3.	10 cc As_2O_3 + 5 cc $K_2Cr_2O_7$ + 10 cc H_2SO_4	10.3	Does not fade
4.	5 cc $Na_2C_4H_4O_6$ + 5 cc $K_2Cr_2O_7$ + 10cc H_2SO_4 (after chromic acid was reduced)	16.6 (in 1 hr.)	Fades rapidly
5.	10 cc $Na_2C_4H_4O_6$ + 10 cc H_2SO_4	——	Fades slowly

From these titrations it was evident that iodine was slowly reduced by the acid sodium tartrate solution alone, (No. 5).

Further, that this reduction took place much faster if the tartrate solution was first partially oxidized by a small amount of chromic acid as shown by the titration results of solution No. 4. This showed that the solution of the difficulty must lie in the oxidation products of the tartrate or the reduction products of the chromate. This was tested by noting the time required for the reduction of a limited amount of iodine by solutions of sodium tartrate and sulphuric acid containing small amounts of the oxidation products of tartaric acid such as, oxalic acid, formic acid and glycollic acid. No particular one of these could be said to cause the fading end-point altho they all served to make the tartrate a bit more easily oxidized by the iodine. The addition of chromic sulphate had little or no effect on the time required for the reduction of the iodine. There remains a possibility that glycollic aldehyde may be the material which caused the trouble; however none could be obtained and this test has been necessarily omitted. Bunsen and Roscoe[1] in their article on "Photo-Chemical Researches" investigated the reaction between dilute solutions or bromine and tartaric acid. They noted the auto-catalytic nature of the reaction and concluded from their work that the cause of increase in the speed of the reaction as it progressed did not lie in any peculiarity which light possessed but rather to the mode of action itself. In other words the reaction was autocatalytic because of chemical induction and not because of photo-induction. They however did not try to explain the cause of this chemical induction.

It was possible however to do away with the fading end-point as far as concerned in this particular investigation by a slight change in procedure. Namely, by working always with an excess of chromic acid and thus making it unnecessary to titrate arsenious acid in the presence of partially oxidized tartaric acid. This procedure proved to be satisfactory and was used in all the remaining experiments.

Direct Oxidation of Sodium Tartrate by Chromic Acid

The oxidation of sodium tartrate was carried out at various temperatures, 100°, 72° and 22° (room temperature) in order to determine the amount of oxygen taken up per mol of sodium tartrate. The reaction was allowed to run for a definite time after which the excess chromic acid was determined by adding potassium iodide and sulphuric acid, and titrating the iodine liberated with standard sodium thiosulphate. The oxidation at 100°C was carried out by boiling the reaction mixture under a reflux condenser for the required time after which it was cooled in ice water for five minutes, then titrated immediately. For the oxidation at 72°C the reaction mixture was brought to 72°C in boiling water as quickly as possible after mixing, then placed in a drying oven and held at that temperature. At the end of the required time it was cooled in ice water for five minutes and then the excess chromic acid was titrated immediately.

Fig. 2a, b and c shows the variation in the amount of oxygen used per mol of sodium tartrate, per unit time at the various temperatures as given in Table III. From this work it was apparent that the speed of the reaction

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[1] Bunsen and Roscoe: Phil. Trans., **147**, 399 (1857).

TABLE III

Reaction Mixture: 5 cc M/100 $Na_2C_4H_4O_6$; 10 cc M/10 H_2SO_4 and 50 cc M/100 $K_2Cr_2O_7$

Pt. 1 Oxidation at 100°C.

No.	Time in hrs.	Excess $K_2Cr_2O_7$	$K_2Cr_2O_7$ used	Oxygen used per Mol. Tart.
1	1/2	43.31	6.69	0.67
2	1	32.75	17.25	1.72
3	2	21.6	28.4	2.8
4	6	15.75	34.25	3.48
5	12	13.70	36.3	3.63
6	24	12.46	37.54	3.75
7	48	10.3	39.7	3.96

Pt. 2 Oxidation at 72°C.

No.	Time in hrs.	Excess $K_2Cr_2O_7$	$K_2Cr_2O_7$ used	Oxygen used per Mol. Tart.
1	1/2	49.28	0.72	0.07
2	1	48.37	1.63	0.16
3	2	44.41	5.59	0.56
4	6	33.88	16.12	1.61
5	12	17.34	32.66	3.26
6	24	16.02	33.98	3.4
7	48	15.31	34.69	3.47
8	62	14.5	35.5	3.54
9	86	13.99	36.01	3.6

Pt. 3 Oxidation at 22°C (Room Temp.)

No.	Time in hrs.	Excess $K_2Cr_2O_7$	$K_2Cr_2O_7$ used	Oxygen used per Mol. Tart.
1	2	49.79	0.21	0.021
2	12	49.28	0.72	0.07
3	24	48.47	1.53	0.15
4	48	43.6	6.4	0.63
5	60	39.14	10.86	0.96
6	77	35.18	14.82	1.48
7	100	28.90	21.1	2.1
8	432	19.57	30.43	3.04

between chromic acid and tartaric acid was considerably decreased by a lowering of the temperature. Further, that under these conditions four atoms of oxygen was the maximum used per mol of sodium tartrate; or, at least, the number of atoms of oxygen used per mol of sodium tartrate approached four as a limit, which meant that the tartrate was oxidized toward oxalate. At room temperature, however, the reactions became distinctly autocatalytic and much slower. The induction period lasted for several hours, the speed of the reaction gradually increased until nearly two atoms of oxygen were used per mol of sodium tartrate and then began to decrease. In other words glycollic acid was the turning point in the speed of the oxidation.

The fact that the oxidation of tartaric acid by chromic acid was autocatalytic in nature was thought to be in some way connected with the fading end-point previously obtained with iodine titrations in partially oxidized tartrate solutions. Further, since the oxidation of tartaric acid by bromine was autocatalytic as shown by Bunsen and Roscoe,[1] it seemed that the explanation must lie in the oxidation products of the tartrate. The catalytic effect of glycollic acid, oxalic acid, formic acid and chromic sulphate was tried on the oxidation of tartrate using chromic acid as the oxidizing agent instead of iodine as previously tried. The excess chromic acid was determined after five hours when 25 cc of N/100 $K_2Cr_2O_7$ was added to a mixture of 5 cc M/20 $Na_2C_4H_4O_6$, 10 cc 4N H_2SO_4 and 0–10 cc M/10 supposed catalyst. In no case however, was the amount of chromic acid used changed by a variation in the amount of supposed catalyst, which of course eliminated them as possible autocatalysts for this reaction. It was known from the researches of Harcourt and Esson[2] and later by Skrabal[3] that in the oxidation of oxalic acid by potassium permanganate manganous sulphate was found to be the autocatalyst. Hence, could chromous sulphate, the corresponding salt in the above reaction, be the autocatalyst? This was investigated by reducing a M/10 solution of chromic sulphate in a Jones reductor, then testing the catalytic effect of the chromous sulphate thus formed on the oxidation of tartrate by chromic acid.—It should perhaps be mentioned that chromous sulphate is unstable in air and is gradually oxidized back to chromic sulphate. It was therefore possible to obtain the effect of decreasing chromous sulphate concentration by making runs at different time intervals after the chromic sulphate had been reduced.

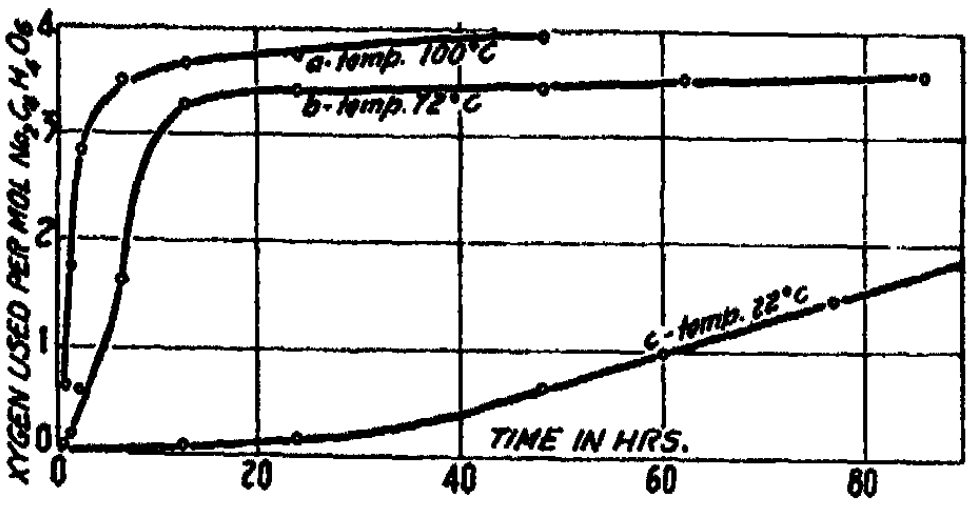

Fig. 2 a, b and c

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[1] Loc. cit.

[2] Harcourt and Esson: J. Chem. Soc., 20, 460 (1867).

[3] Skrabal: Z. anorg. Chem., 42, 1 (1904).

TABLE IV

Mixture put thru Jones reductor in order mentioned; 100 cc N H_2SO_4, 50 cc M/10 $Cr_2(SO_4)_3$, 200 cc N H_2SO_4 and 100 cc H_2O. Total vol. 450 cc. Acidity of resulting chromous sulphate solution determined by titrating with standard sodium hydroxide—.6 Normal.

Reaction Mixture: 50 cc N/100 $K_2Cr_2O_7$, 5 cc M/100 $Na_2C_4H_4O_6$ and 2 cc of chromous sulphate solution taken at various time intervals after the reduction as indicated.

Temp. 22°C (Room) 40 cc N/100 $K_2Cr_2O_7$ = 40 cc N/100 $Na_2S_2O_3$

Pt. 1 Time after reduction, 5 min. 2 cc $CrSO_4$ = 2.7 cc. $K_2Cr_2O_7$

No.	Time in hrs.	$Na_2S_2O_3$ Titre	$K_2Cr_2O_7$ used
1	1	47.1	2.9
2	4	46.25	3.75
3	9	44.7	5.3
4	22	39.5	10.5
5	33	35.2	14.8

Pt. 2 Time after reduction, about 12 hrs. 2 cc $CrSO_4$ = .4 cc $K_2Cr_2O_7$

No.	Time in hrs.	$Na_2S_2O_3$ Titre	$K_2Cr_2O_7$ used
1	1	49.6	0.4
2	12	47.1	2.9
3	23	42.8	7.2
4	36	37.3	12.7
5	45	34.4	15.6

Pt. 3 Time after reduction, about 48 hrs. 2 cc $CrSO_4$ = 0cc $K_2Cr_2O_7$

No.	Time in hrs.	$Na_2S_2O_3$ Titre	$K_2Cr_2O_7$ used
1	4	50	0.0
2	8	49.6	0.4
3	24	47.	3.
4	33	43.3	6.7
5	48	37.6	12.4

The results obtained as shown in Table IV and represented by Fig. 3 showed that chromous sulphate without question hastened the oxidation of tartrate by chromic acid. Whether this was caused by the chromous sulphate acting as an autocatalyst or by the formation of a lower and more active stage of chromic acid, due to the presence of the chromous sulphate, one could not be certain as either would serve to explain the above results. Since almost any strong reducing agent may cause chromic acid to react more rapidly on tartrate and further, since the oxidation of tartrate by bromine is a reaction of the same character, it seems that the real autocatalyst must be some oxidation product of the tartrate which is a strong reducing agent. These requirements would be fulfilled by glycollic aldehyde. This was not tested however, for the reason that none could be obtained, as previously stated.

Knowing that the direct oxidation of tartaric acid was autocatalytic it seemed quite probable that the induced oxidation of the tartrate in the presence of arsenious acid was simply a case of catalysis. In other words the arsenious acid must serve to do away with the inductive period in the direct oxidation of the tartrate by the chromic acid. If this were true according to the theory, Case 1, the induction factor should increase indefinitely with a relative increase in the concentration of tartrate to arsenite in case one added chromic acid (A) to a mixture of arsenious acid and tartaric acid (B) and (C) instead of reaching a limited value as indicated by Schilow's work.

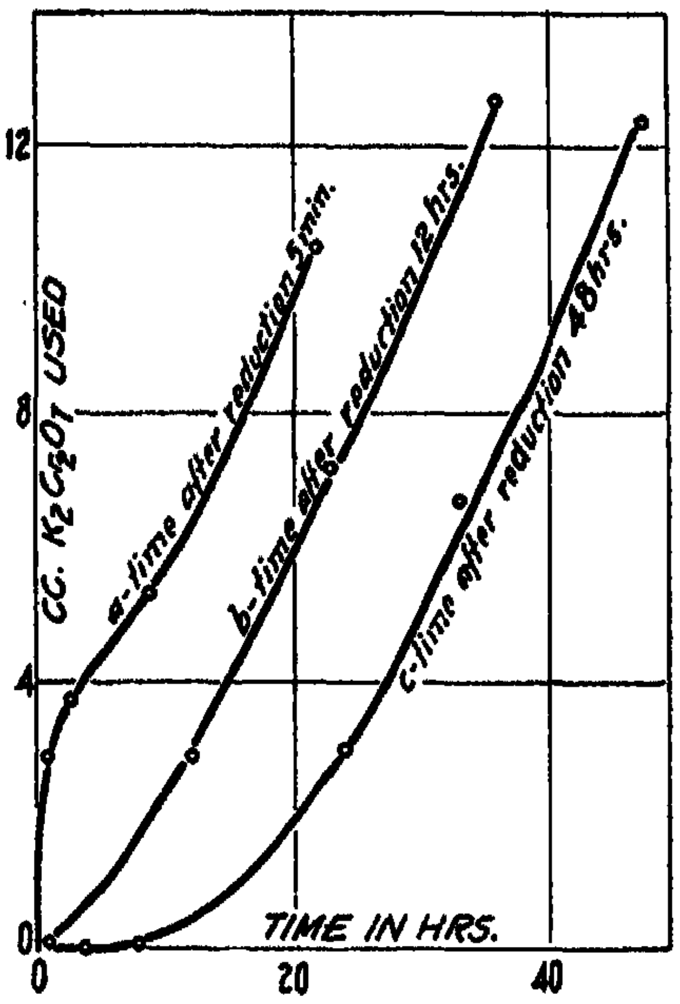

FIG. 3

Variation of Induction Factor with Arsenious Acid Conc. and Time

Using an excess chromic acid, an attempt was made to increase the induction factor obtained by Schilow for the M/100 tartrate solution. It was thought best to increase the ratio of the concentration of tartaric acid to arsenious acid by decreasing the amount of arsenious acid used rather than by increasing the concentration of the tartaric acid as this would make it unnecessary to work with such concentrated solutions. The reaction was allowed to run for a time sufficient to oxidize all the arsenious acid present. The oxidation of 5 cc N/100 As_2O_3 solution by 10 cc N/100 $K_2Cr_2O_7$ in the presence of 10 cc N/10 H_2SO_4 was found to be complete in the course of about one hour by special experiment. When the reaction had run for the stated time 10 cc of approx. 2N KI and 10 cc of approx. 4N H_2SO_4 were added, after three minutes the iodine liberated by the excess chromic acid was titrated with N/100 $Na_2S_2O_3$.

TABLE V

Reaction Mixture: 50 cc N/100 $K_2Cr_2O_7$, 10 cc N/10 H_2SO_4, 5 cc M/100 $Na_2C_4H_4O_6$ and—cc N/100 As_2O_3

Temp. 22°C (Room).

Pt. 1 Time given for reaction 2 hrs.

No.	cc As_2O_3	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	Ind. Factor	$\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$
1	5	30.85	14.15	2.82	20
2	2	39.65	8.35	4.15	50
3	1	44.05	5.	5.	100
4	1/2	46.8	2.7	5.4	200
5	1/10	49.3	.6	6.	1000
6	0	49.95	—	—	—

Pt. 2 Time given for reaction 3 hrs.

No.	cc As_2O_3	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	Ind. Factor	$\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$
1	5	30.1	14.9	2.98	20
2	2	38.55	9.5	4.75	50
3	1	43.15	5.8	5.8	100
4	1/2	46.1	3.4	6.8	200
5	1/10	49.1	.8	8.	1000
6	0	50.1	—	—	—

Pt. 3 Time given for reaction 38 hrs.

No.	cc As_2O_3	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	Ind. Factor original	Ind. Factor corrected	$\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$
1	5	21.5	23.5	4.1	3.88	20
2	2	26.3	21.7	10.8	8.8	50
3	1	28.5	20.5	20.5	17.4	100
4	1/	31.2	18.3	36.3	28.4	200
5	1/10	38.3	11.6	116.	75	1000
6	0	45.9	4.1	—	—	—

In Table V the amount of chromic acid used by the inductor (arsenious acid) was exactly equal to the amount of arsenious acid used in the different experiments. The corrected induction factor as given in pt. 3, Table V, was obtained by subtracting from the total amount of chromic acid used by the acceptor in each respective run, the amount of chromic acid used when no inductor was present, 4.1 cc. and dividing this result by the amount of chromic acid used by the inductor. This was considered the apparent correction for the voluntary oxidation of the tartaric acid by the chromic acid.

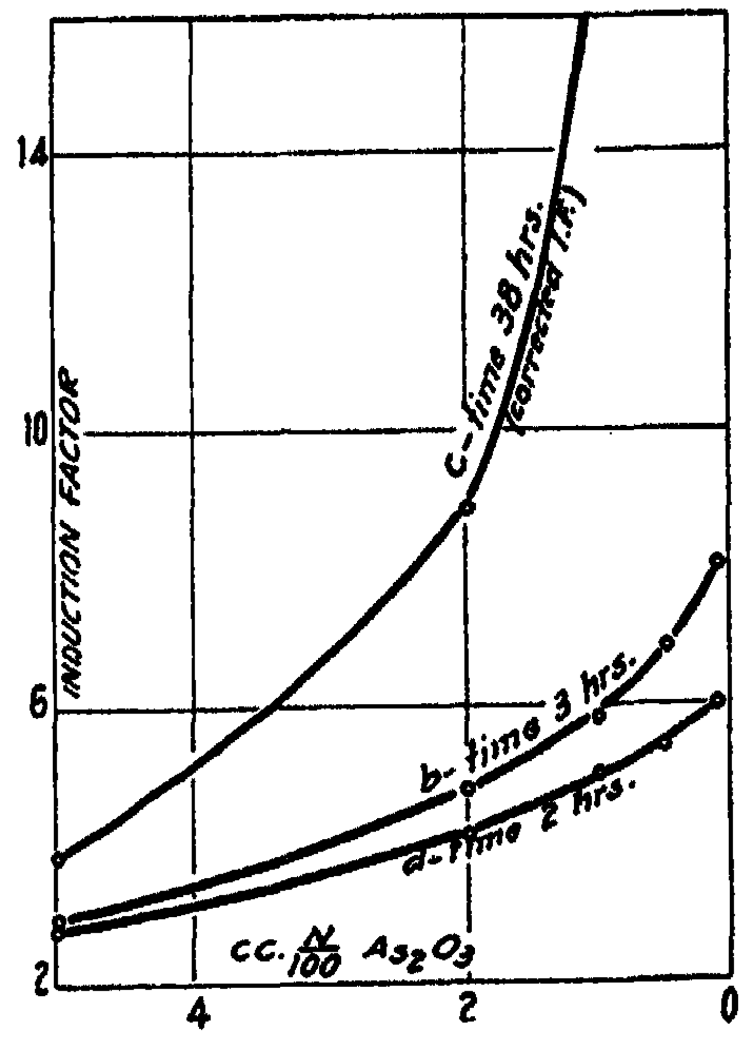
14
10
6
2
INDUCTION FACTOR
c-time 38 hrs. (corrected I.F.)
b-time 3 hrs.
a-time 2 hrs.
cc. N/100 As2O3
4
2
0

Fig. 4

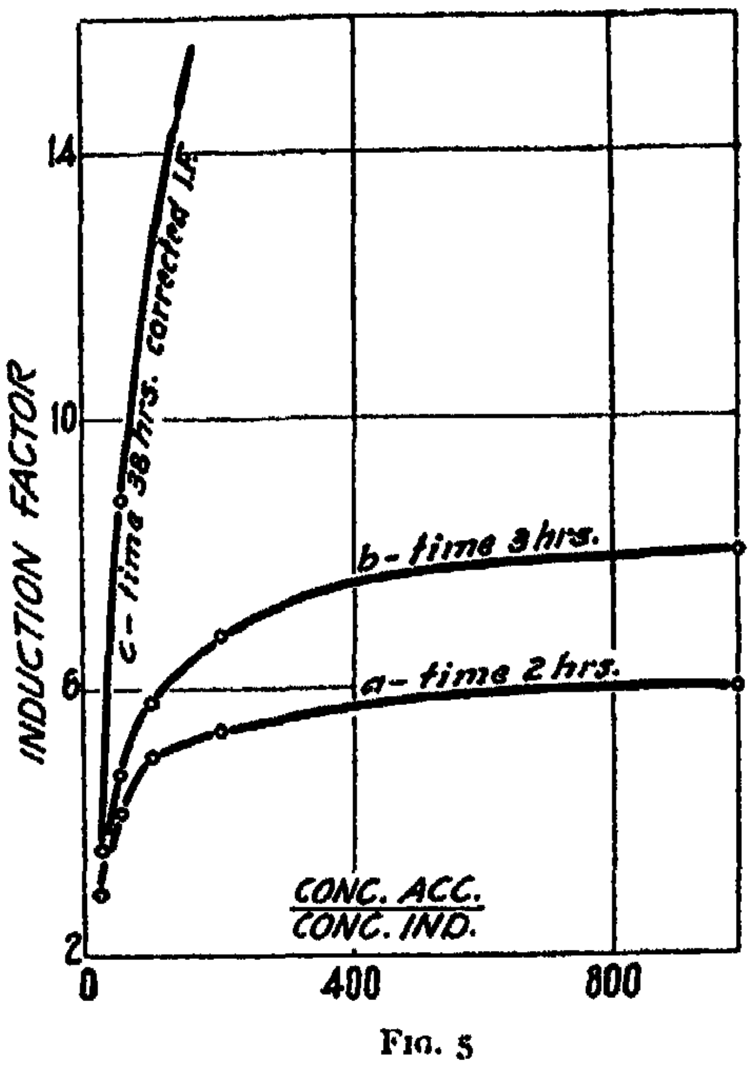
14
10
6
2
INDUCTION FACTOR
c-time 38 hrs. corrected I.F.
b-time 3 hrs.
a-time 2 hrs.
CONC. ACC. / CONC. IND.
0
400
800

Fig. 5

Figs. 4 and 5 show how the induction factor varied with the amount of arsenious acid used and the ratio $\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$ respectively. It was thought at first that this solved the problem and that the arsenious acid was merely playing the part of a catalyst, since the induction factor could be increased almost indefinitely by increasing the ratio of the concentration of the acceptor to the inductor. However on further consideration it became apparent that, if the arsenious acid was taking the part of a catalyst, these curves should coincide provided proper correction per unit time was made for the voluntary oxidation of tartaric acid by chromic acid.

There were two possible ways of making this correction. Either develop and apply the proper mathematical equations or eliminate the reaction between the chromic acid and the tartaric acid by working at a lower temperature, as this reaction has always been shown to be quite sensitive to temperature changes. After due consideration the latter method was selected as the one most likely to give correct results provided lowering the temperature did not slow down the reaction between the chromic acid and the arsenious acid too much. This was investigated however, at 1°C and it was found that the rate of oxidation of arsenious acid was only slightly affected, 5 cc N/100 As_2O_3 + 10 cc N/10 H_2SO_4 being completely oxidized by 10 cc N/100 potassium dichromate in two hours. An attempt was therefore made to eliminate the voluntary oxidation of the tartrate by the chromic acid by working at this temperature.

Variation of the Induction Factor at 1°C

First, Effect of Time: The reaction was allowed to take place in an insulated ice bath. Potassium dichromate was added to a mixture of arsenious acid, sodium tartrate and sulphuric acid. After the reaction had run for the desired time the excess chromic acid was determined by titration in the same manner as previously described.

From the results of these experiments as shown by Table VI A it became apparent that at this temperature the voluntary oxidation of the tartrate by

TABLE VI A

Reaction Mixture: 25 cc N/100 $K_2Cr_2O_7$, 5 cc M/100 $Na_2C_4H_4O_6$, 2 cc N/100 As_2O_3 and 10 cc N/10 H_2SO_4. Temp. 1°C.
10 cc $K_2Cr_2O_7$ = 10 cc As_2O_3 = 10 cc $Na_2S_2O_3$.
2 cc $K_2Cr_2O_7$ used by Inductor in each case.

					Corrected 2 cc per hr.	
No.	Time in hrs.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	cc $K_2Cr_2O_7$ used by Acc.	I.F.
1	2	17.6	5.4	2.7	5	2.5
2	3	17.3	5.7	2.85	5.1	2.55
3	4	17.1	5.9	2.95	5.1	2.55
4	5	16.8	6.2	3.1	5.2	2.6
5	16	14.7	8.3	4.15	5.1	2.55

the chromic acid was not quite eliminated but continued using about 0.2 cc of the potassium dichromate solution per hour. This correction, when applied as shown by the last two columns of the table, gave a fairly constant induction factor of 2.5. It was thought best not to run the temperature of the bath lower because of the possibility of freezing the solutions but to determine the maximum induction factor at 1°C making the necessary corrections for the small amount of voluntary tartrate oxidation which took place.

Second, Effect of Sodium Tartrate Concentration: The same reaction mixture was used as above with the exception that the concentration of the sodium tartrate was varied as indicated in order to find what concentration was necessary to give the highest possible induction factor. The time allowed for the reaction to take place was three hours.

TABLE VI B

Pt. 1 = 0.1N H_2SO_4 used (same as in VI A)

No.	$Na_2C_4H_4O_6$ Conc.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F. (uncorrected)
1	M/100	17.4	5.6	2.8
2	M/50	16.	7.	3.5
3	M/20	15.1	7.9	3.95
4	M/10	17.15	5.85	2.92
5	M/5	17.55	5.45	2.72

Pt. 2 — .4N H_2SO_4 used.

No.	$Na_2C_4H_4O_6$ Conc.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F. (uncorrected)
1	M/100	17.2	5.8	2.9
2	M/50	15.1	7.9	3.95
3	M/20	12.1	10.9	5.4
4	M/10	9.9	13.1	6.55
5	M/5	7.6	15.4	7.7

When N/10 H_2SO_4 was used, a maximum induction factor was obtained with M/20 sodium tartrate as shown by Pt. 1 of Table VI.B and Fig. 6a. It was then necessary to explain the cause of this maximum. After some investigation the cause was finally located in the acidity of the reaction mixture. Pt. 2 of Table B and Fig. 6b show the same runs as in the previous case using 0.4N H_2SO_4 in place of the 0.1N H_2SO_4 from which it can be seen that the maximum induction factor with increasing tartrate concentration has been eliminated. This made it clear that the reason why the induction factor passed through a maximum in the previous case with increasing sodium tartrate concentration was because of decreased acidity which would cause a corresponding decrease in the oxidation potential of the chromic acid and hence less chromic acid would be used per unit of time. This brought to our attention another factor which had not as yet received much consideration namely, acid concentration.

Third, Effect of Acid Concentration: The original reaction mixture was used in so far as was possible and the effect of acid concentration was investigated at two different sodium tartrate concentrations. The time allowed for the reaction was kept at three hours.

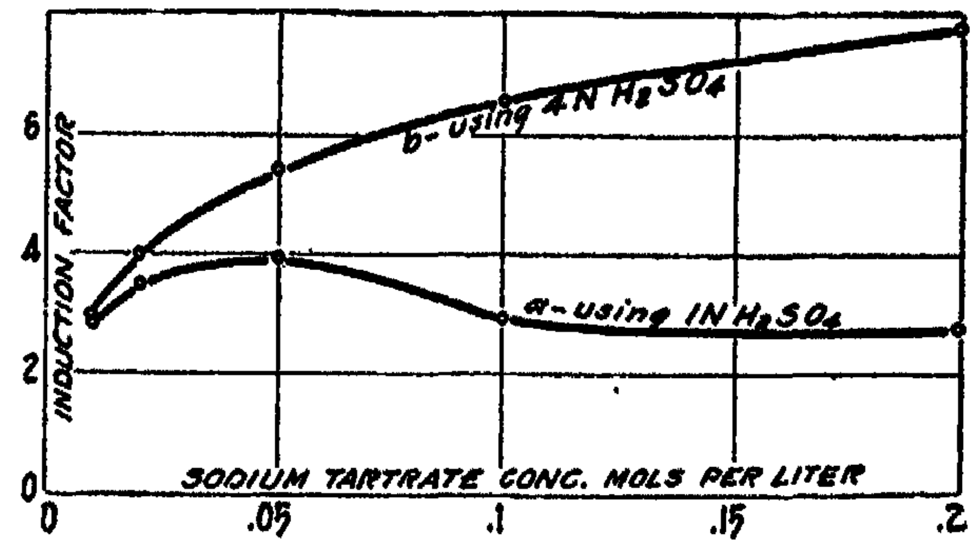

Fig. 6 a and b

Table VI C

Pt. 1 M/100 $Na_2C_4H_4O_6$ used (same as in VI A)

No.	H_2SO_4 Conc.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F. (uncorrected)
1	0.1N	17.25	5.75	2.87
2	0.2N	17.2	5.8	2.9
3	0.4N	17.	6.	3.
4	0.6N	17.2	5.8	2.9
5	0.8N	17.7	5.3	2.65
6	N	18.6	4.4	2.2

Pt. 2 M/20 $Na_2C_4H_4O_4$ used.

No.	H_2SO_4 Conc.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F. (uncorrected)
1	0.1N	15	8.	4
2	0.2N	13.5	9.5	4.75
3	0.4N	12	11	5.5
4	0.6N	11	12	6
5	0.8N	10.3	12.7	6.3
6	N	9.7	13.3	6.65

Using M/100 sodium tartrate the induction factor was observed to pass thru a maximum when 0.4N H_2SO_4 was used as shown by pt. 1, Table VI C and Fig. 7a. When a more concentrated M/20 sodium tartrate solution was used however no maximum was obtained with increasing acid concentration, pt. 2, Table VI C and Fig. 7b. It however seems quite possible that at sufficiently high acid concentrations this curve might also pass thru a maximum, provided the voluntary oxidation of the tartrate by the chromic acid did not become too pronounced. Be that as it may, the fact remains that a maximum such as was obtained in the first case was somewhat of a mystery and the explanation did not become apparent until considerably more research had been done. It would naturally be expected that as the acidity was increased the oxidation potential of the chromic acid would be increased and therefore more chromic acid would be used per unit of time due to increased reaction velocity. Such was not the case however and the reason was because some other factor had entered into the reaction which decreased the amount of chromic acid used as the acidity was increased. Later work on the solubility of arsenious oxide in sodium tartrate made acid with tartaric acid has shown the distinct probability of the formation of an unstable complex between undissociated sodium tartrate and arsenious acid, also the improbability of such a complex between tartaric acid and arsenious acid. If we accept for the time being that such a complex exists then the above maximum has an apparent explanation, as increasing the acidity would cause the removal of tartrate ions, therefore further dissociation of the sodium tartrate, and the formation of more and more undissociated tartaric acid. This would mean a decrease in the amount of the sodium tartrate-arsenious acid complex and therefore less induced oxidation of the tartrate, as well as, less chromic acid used per unit of time provided the voluntary oxidation of the tartrate was not too great as might well be the case at very high acid concentration.

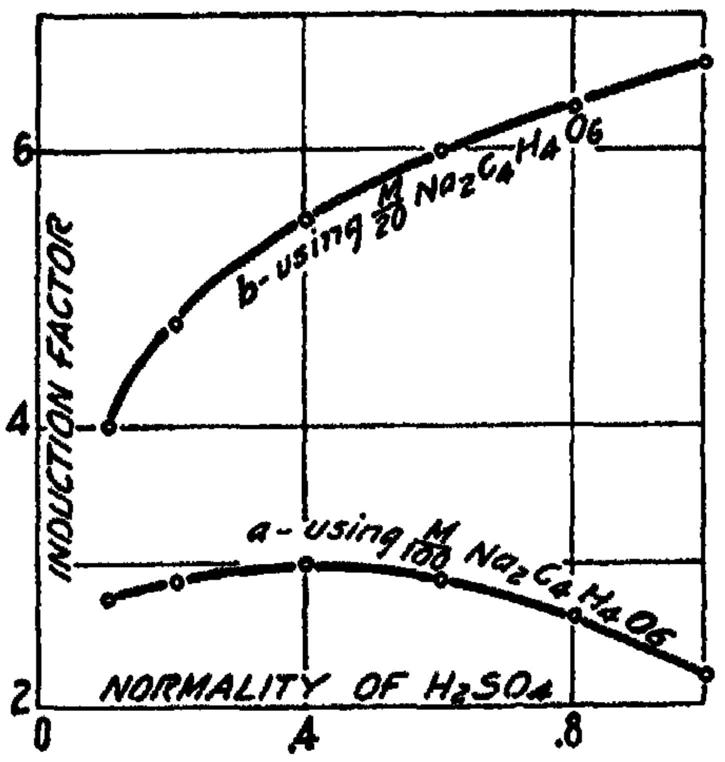

Fig. 7 a and b

Determination of the True Limited Induction Factor

Considering the above results it seemed that the highest limited value of the induction factor should be obtained if M/20 sodium tartrate and 0.4N sulphuric acid were used in the above reaction mixture since these concentrations gave the maximum rate of oxidation in the previous experiments. The correction for voluntary oxidation of the tartrate by the chromic acid was of course determined by the amount of chromic acid used per unit of time after all the arsenious acid had been oxidized.

It may be seen from the above Table VII that a constant limited induction factor of 4 was obtained for two concentrations of arsenious acid which showed that the induction factor really was independent of the arsenite concentration and hence the ratio of the concentration of the acceptor to that of the inductor, within these limits, provided proper correction was made for voluntary oxidation. In other words the induction factor did not increase with an increase in the ratio $\frac{\text{Conc. Acc.}}{\text{Conc. Ind.}}$ as has been previously indicated. However, before this could be accepted as the true limited induction factor, it was considered necessary to determine the induction factor, making proper corrections in reaction mixtures, using a higher acid concentration, a lower acid concentration and a mixture using both a higher acid and tartrate concentration. The induction factor obtained in each case after correction for voluntary oxidation however, was found to be lower than 4 as shown by Table VIII. This made it reasonably certain the 4 was the actual limited induction factor for this reaction rather than 2.8 as determined by Schilow.

TABLE VII

Reaction Mixture: 25 cc N/100 $K_2Cr_2O_7$, 10 cc. .4N H_2SO_4, 5 cc M/20 $Na_2C_4H_4O_7$

Pt. 1 — 2 cc N/100 As_2O_3 used. Temp. 1° V.

No.	Time in hrs.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	Corrected 1 cc per hr.	
					cc $K_2Cr_2O_7$ used by Acc.	I.F.
1	2	12.9	10.1	5.05	8.1	4.05
2	3	11.9	11.1	5.55	8.1	4.05
3	4	10.95	12.05	6.025	8.05	4.25
4	5	9.9	13.1	6.55	8.1	4.05

Pt. 2 — 1 cc N/100 As_2O_3 used.

No.	Time in hrs.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	Corrected 1.03 cc per hr.	
					cc $K_2Cr_2O_7$ used by Acc.	
1	2	17.87	6.13	6.13	4.07	4.07
2	3	16.82	7.18	7.18	4.09	4.09
3	4	15.77	8.23	8.23	4.11	4.11
4	5	14.75	9.25	9.25	4.1	4.1

The induction factor of 4 as obtained above ruled out the possibility that the inductor (arsenious acid) acted as a catalyst as was first suspected when the direct oxidation of the tartrate was found to be autocatalytic. There still remained the possibility that a lower stage of chromic acid was formed which then reacted with the tartaric acid, Case 2. Since glycollic acid was

TABLE VIII

Pt. 1 Reaction Mixture: 25 cc N/100 $K_2Cr_2O_7$, 2 cc N/100 As_2O_3, 10 cc N/10 H_2SO_4 and 5 cc M/20 $Na_2C_4H_4O_6$. Temp. 1°C.

					Corrected .2 cc per hr.	
No.	Time in hrs.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	cc. $K_2Cr_2O_7$ used by Acc.	I.F.
1	2	15.2	7.8	3.9	7.4	3.7
2	3	15.	8.	4.	7.4	3.7
3	4	14.8	8.2	5.1	7.4	3.7
4	5	14.55	8.45	4.22	7.45	3.72
5	6	14.4	8.6	4.3	7.4	3.7

Pt. 2 Reaction Mixture: 25 cc N/100 $K_2Cr_2O_7$, 2 cc N/100 As_2O_3, 10 cc. 8NH_2SO_4, 5 cc M/20 $Na_2C_4H_4O_6$. Temp. 1°C.

					Corrected 1.6 cc per hr.	
No.	Time in hrs.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	cc $K_2Cr_2O_7$ used by Acc.	I.F.
1	2	12.3	10.7	5.35	7.5	3.75
2	3	10.6	12.4	6.2	7.6	3.8
3	4	8.75	14.25	7.12	7.85	3.92
4	5	7.35	15.65	7.82	7.65	3.82
5	6	6.75	16.75	8.37	7.55	3.77

Pt. 3 Reaction Mixture: 25 cc N/100 $K_2Cr_2O_7$. 2 cc N/100 As_2O_3, 10 cc .6N H_2SO_4 and 5 cc M/10 $Na_2C_4H_4O_4$. Temp. 1°C.

					Corrected .8 cc per 15 min.	
No.	Time in min.	$Na_2S_2O_3$ Titre	cc $K_2Cr_2O_7$ used by Acc.	I.F.	cc $K_2Cr_2O_7$ used by Acc.	I.F.
1	5	16	7	3.5	6.7	3.35
2	15	14.4	8.6	4.3	7.8	3.9
3	30	13.6	9.4	4.7	4.7	3.9
4	45	12.8	10.2	5.1	7.8	3.9
5	1 hr.	11.9	11.1	5.55	7.9	3.95

less readily oxidized than tartaric acid or at least was more slowly oxidized as shown by the direct oxidation of sodium tartrate with chromic acid at room temperature, Table III Fig. 2, the induction factor 4 might be explained by means of a lower stage of chromic acid as follows:

Let T = Tartaric Acid; TO = Glycollic Aldehyde; TO_2 = Glycollic Acid. (Glycollic aldehyde is a stronger reducing agent than tartaric acid and it was assumed to react promptly with chromic acid.)

$$3As_2O_3 + 6Cr_2O_6 = 3As_2O_5 + 6Cr_2O_5$$

$$6Cr_2O_5 + 12T = 6Cr_2O_3 + 12TO$$

$$4Cr_2O_6 + 12TO = 4Cr_2O_3 + 12TO_2$$

$$12 + 12/6 = 4 \text{ induction Factor.}$$

The only other explanation of a limiting induction factor of 4 for this reaction would be the formation of a tartaric acid-arsenious acid complex, Case 4, as was postulated by Schilow. This however seemed improbable since the inductor has been shown to be non-specific. However as a further test it was decided to determine the induction factor for the oxidation of tartaric acid, in the presence of arsenious acid, by permanganic acid instead of chromic acid. If a complex were formed between the tartrate and the arsenite we should expect to get the same limiting induction factor regardless of the oxidizing agent (actor) used, provided all other conditions were constant.

Permanganic Acid, Arsenious Acid, Tartaric Acid

Before an attempt could be made to determine the true limited induction factor for this reaction using potassium permanganate instead of potassium dichromate it was necessary to carry out a few preliminary experiments in order to determine the nature of this reaction.

Direct Oxidation of Sodium Tartrate by Permanganic Acid

These experiments were run at room temperature and the same analytical methods were employed to determine the excess permanganic acid as were previously used to determine the excess chromic acid. The results obtained are shown by Table IX and Fig. 8 from which it may be observed that the oxidation of tartrate by permanganic acid was quite similar to its oxidation with chromic acid. The reaction was autocatalytic and the oxygen consumed per mol approached four as a maximum value. In general however the rate of the oxidation was somewhat more rapid than when chromic acid was used as would be expected since permanganic acid is a much stronger oxidizing agent.

TABLE IX

Reaction Mixture: 50 cc N/100 $KMnO_4$, 5 cc M/100 $Na_2C_4H_4O_6$ and 10 cc N/10 H_2SO_4. Temp. 22°C (Room)

10 cc N/100 $Na_2S_2O_3$ = 10 cc N/100 $KMnO_4$

No.	Time in hrs. and min.	$Na_2S_2O_3$ Titre	cc $KmnO_4$ used by Tartrate	Oxygen used per mol of Sodium Tartrate
1	1 hr.	49.24	.66	0.06
2	1 hr. 20 min.	46.38	3.52	0.35
3	1 hr. 40 min.	31.72	18.18	1.8
4	2 hr.	25.6	24.4	2.4
5	2 " 10 min.	22.9	27.1	2.7
6	2 " 20 min.	21.18	28.72	2.87
7	2 " 30 "	20.28	29.62	2.96
8	3 hr.	18.67	31.23	3.1
9	5 "	17.16	32.24	3.27
10	6 "	16.76	33.14	3.3
11	19 "	13.95	36.05	3.6
12	115 "	7.9	42.1	4.2

Method of Analysis and Correction for Voluntary Oxidation

A number of experiments were run in order to determine whether the necessary correction to be applied for the voluntary oxidation of the tartrate by the permanganate could be found in the same manner as in the previous reaction using chromic acid, namely, by finding the amount of permanganate used per unit of time after all of the arsenious acid had been oxidized. The time required for the complete oxidation of arsenious acid at such concentrations as used in the experiments was found to be five to ten minutes.

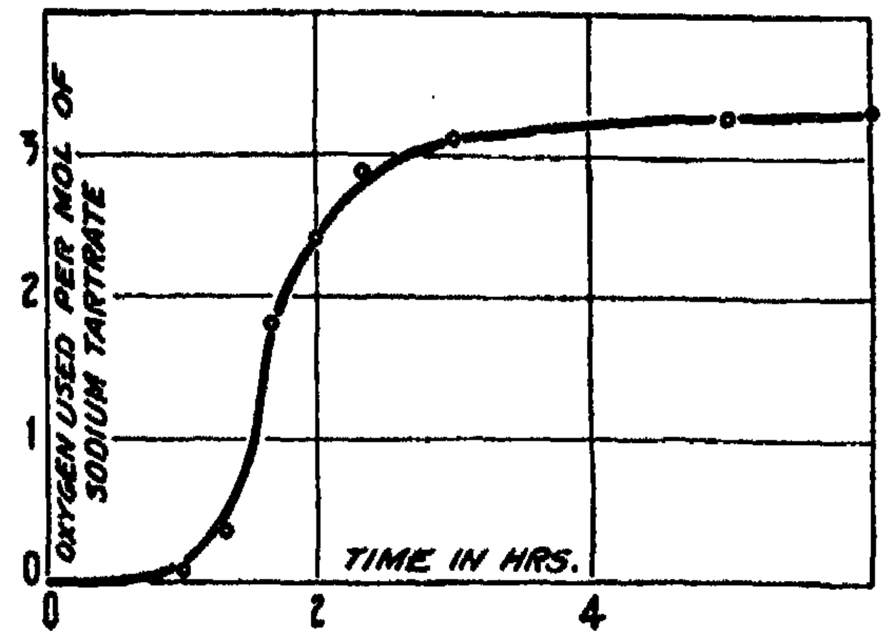

FIG. 8

TABLE X

Pt. 1 Reaction Mixture: 25 cc N/100 $KMnO_4$; 5 cc N/20 $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3 and 10 cc .4N H_2SO_4.

					Corrected .8 cc per 10 min.	
No.	Time in min.	$Na_2S_2O_3$ Titre	cc $KMnO_4$ used by Acc.	I.F.	cc $KMmO_4$ used by Acc.	I.F.
1	5	19.5	3.5	1.7	3.1	1.55
2	10	19.1	3.9	1.95	3.1	1.55
3	20	18.3	4.7	2.35	3.1	1.55
4	30	17.4	5.6	2.8	3.2	1.6
5	60	15.05	7.95	3.99	3.15	1.57
Pt. 2	M/10 $Na_2C_4H_4O_6$ used.					
2	5	19	4	2	3.4	1.7
2	10	18.35	4.65	2.32	3.45	1.77
3	20	17.3	5.7	2.85	3.3	1.65
4	30	16.1	6.9	3.45	3.3	1.65
5	40	14.8	8.2	4.1	3.4	1.7

The titration for excess permanganate was made in the manner as for excess dichromate with the exception that care had to be taken in this case, that the solution to be titrated was not made too strongly acid as very strongly acid tartrate solutions were found to liberate iodine from potassium iodide.

Potassium permanganate was first substituted for potassium dichromate in the reaction mixture which previously gave the highest induction factor, the same concentrations being used thruout.

The results obtained as shown by Table X were fairly constant and satisfactory with the exception that the reaction was so rapid that it was rather difficult to obtain exceedingly accurate results. Nevertheless, the results obtained above were believed to be of sufficient accuracy to warrant continuation of the investigation using the same method to correct for voluntary oxidation. The corrected induction factor obtained with permanganate, Pt. 1, Table X, was 1.55 while a corrected induction factor of 4 was obtained with dichromate in the same reaction mixture. It became apparent however on further investigation that 1.55 was not the highest possible induction factor for the permanganate reaction for when the experiments were repeated using a somewhat more concentrated sodium tartrate solution, Pt. 2, Table X, a corrected induction factor of about 1.7 was obtained. This of course showed the necessity of making a study of the effective concentration for the various components of the reaction in order to determine what particular reaction mixture would give the highest possible corrected induction factor.

Variation of the Induction Factor at 1°C

First, Effect of Sodium Tartrate Concentration; The variation of the induction factor with sodium tartrate concentration was investigated in two reaction mixtures which differed only in the amount of arsenious acid present. The object of the experiments was of course to determine what

TABLE XI

Pt. 1—Reaction Mixture: 25 cc N/100 $KMnO_4$, 2 cc N/100 As_2O_3, 10 cc 0.4N H_2SO_4 and $Na_2C_4H_4O_6$ (as indicated).

Time of Reaction—5 min. Temp. 1°C.

10 cc As_2O_3 = 10 cc $KMnO_4$ = 10 cc $Na_2S_2O_3$.

No.	$Na_2H_4O_6$ Conc.	$Na_2S_2O_3$ Titre	cc $KMmO_4$ used by Acc.	I.F. (uncorrected)
1	M/100	21.4	1.6	0.8
2	M/100	18.8	4.2	2.1
3	M/5	18	5.	2.5
4	M/2	17.1	6.	3.
5	M	17.8	5.2	2.6

Pt. 2—1 cc As_2O_3 used.

No.	$Na_2C_4H_4O_6$ Conc.	$Na_2S_2O_3$ Titre	cc$KMnO_4$ used by Acc.	I.F (uncorrected)
1	M/100	22.85	1.15	1.15
2	M/10	21.7	2.3	2.3
3	M/5	21.1	2.9	2.9
4	M/2	20.1	3.9	3.9
5	M	20.4	3.6	3.6

particular tartrate concentration would serve to give the highest possible induction factor and whether or not this concentration was affected by the amount of arsenious acid present.

A maximum induction factor was obtained with M/2 $Na_2C_4H_4O_6$ in both reaction mixtures as shown by Table X and Fig. 9. This of course showed the effect of the amount of arsenious acid used to be negligible especially at the concentrations at which it was being employed in the various reaction mixtures as the maximum came at the same tartrate concentration in both of the above cases. A higher induction factor was naturally obtained in Pt. 2 where the lower amount of arsenious acid was used since any voluntary oxidation of the tartrate would be doubly as effective is raising the induction factor as it would be in Pt. 1. The fact that a maximum induction factor was obtained with increasing sodium tartrate concentration was believed to be explained by the same considerations as previously given when chromic acid was used as the oxidizing agent. Namely, with increasing sodium tartrate concentration the rate of oxidation of the tartrate would be increased according to the law of mass action. At the same time, however, the oxidation potential of the permanganate would be lowered due to decreased acidity which would cause a corresponding decrease in the amount of permanganate used per unit of time.

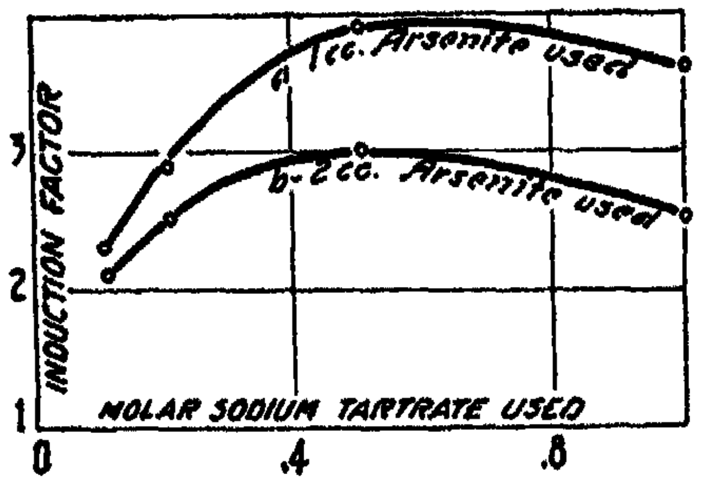

FIG. 9

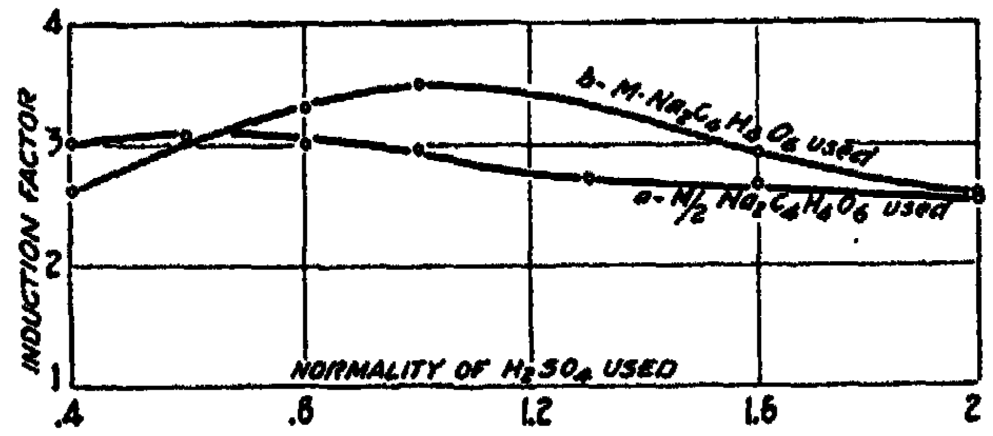

FIG. 10 a and b

Second, Effect of Acid Concentration: The variation of the induction factor with increasing acid concentration was investigated in two reaction mixtures containing different amounts of sodium tartrate as shown in Table XII. When M/2 $Na_2C_4H_4O_6$ was used in the reaction mixture a slight maximum was obtained in the induction factor with .6N H_2SO_4, Pt. 1 Table XII and Fig. 10a. Using M $Na_2C_4H_4O_6$ however, a more distinct maximum was obtained with N H_2SO_4, Pt. 2 Table XII and Fig. 10b. The fact that a maximum induction factor was obtained with increasing acid concentration in both cases was in agreement with the work previously done using the dichromate instead of the permanganate and may be explained in the same manner.

TABLE XII

Pt. 1—Reaction Mixtures: 5 cc M/2 $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3; 25 cc N/100 $KMnO_4$ and 10 cc H_2SO_4 (as indicated).

Time of Reaction – 5 min. Temp. 1°C.

10 cc As_2O_3 = 10 cc $KMnO_4$ = 10 cc $Na_2S_2O_3$

No.	H_2SO_4 Conc.	$Na_2S_2O_3$ Titre	cc $KMnO_4$ used by Acc.	I.F. (uncorrected)
1	0.4	17	6	3
2	0.6	16.85	6.15	3.07
3	0.8	17.	6.	3.
4	1.	17.05	5.95	2.97
5	1.3	17.5	5.5	2.7
6	1.6	17.7	5.3	2.65
7	2.	17.9	5.1	2.5
Pt. 2—Molar—$Na_2C_4H_4O_6$ used.				
1	0.4	17.8	5.2	2.6
2	0.8	16.6	6.6	3.3
3	1.	16.	7.	3.5
4	1.6	17.2	5.8	2.9
5	2.	17.9	5.1	2.55

Determination of the True Limited Induction Factor

The true induction factor must be one which has been corrected for voluntary oxidation of the tartrate by the permanganate. Experiments were run using the reaction mixtures in Table XII which gave maximum induction factors, No. 2 Pt. 1 and No. 3 Pt. 2. The time allowed for the reaction to occur was varied and an attempt was made to determine the amount of permanganate used by direct oxidation of the tartrate per unit of time. This however proved to be successful only in the more dilute reaction mixture as shown in Table XII A.

When M/2 $Na_2C_4H_4O_6$ was used with 0.6N H_2SO_4, Pt. 1 Table XII and Pt. 1—Fig. 11, a corrected induction factor of approximately 3 was obtained. However as shown by Pt. 2 of the same table and figure when Molar $Na_2C_4H_4O_6$ and M H_2SO_4 was used in the reaction mixture a somewhat higher uncorrected induction factor was obtained but the correction to be applied was not constant, decreasing continually with the time of the reac-

TABLE XII A

Pt. 1a—Reaction Mixture: No. 2 Pt. 1 Table XII.

					Corrected .73 cc per 5 min.	
No.	Time in Min.	$Na_2S_2O_3$ Titre	cc $KMnO_4$ used by Acc.	I.F.	cc $KMnO_4$ used by Acc.	I.F.
1	5	16.75	6.25	3.12	5.39	2.69
2	10	15.7	7.3	3.65	5.84	2.92
3	15	15	8.	4.	5.81	2.9
4	20	14.2	8.8	4.4	5.85	2.93
5	25	13.5	9.5	4.75	5.85	2.92

Pt. 1b—1 cc As_2O_3 used.

					Corrected .77 cc per 5 min.	
No.	Time in Min.	$Na_2S_2O_3$ Titre	cc $KMnO_4$ used by Acc.	I.F.	cc $KMnO_4$ used by Acc.	I.F.
1	5	20.15	3.85	3.85	3.08	3.08
2	10	19.3	4.7	4.7	3.16	3.16
3	15	18.5	5.5	5.5	3.19	3.19
4	20	17.8	6.2	6.2	3.12	3.12
5	25	17.	7.	7.	3.15	3.15

Pt. 2a—Reaction Mixture: No. 3 Pt. 2 Table XII

No.	Time in min.	$Na_2S_2O_3$ used	cc $KMnO_4$ used by Acc.	I.F.	Correction in cc per 5 min.
1	3	17.1	5.9	2.95	
2	5	15.7	7.3	3.65	
3	10	14.	9.	4.5	1.7
4	15	12.55	10.45	5.22	1.45
5	20	11.6	11.4	5.7	.9
6	25	10.8	12.2	6.1	.8

Pt. 2b—1 cc As_2O_3 used.

No.	Time in min.	$Na_2S_2O_3$ Titre	cc $KMnO_4$ used by Acc.	I.F.	Correction in cc per 5 min.
1	3	20.6	3.4	3.4	
2	5	19.7	4.3	4.3	
3	10	17.8	6.2	6.2	1.9
4	15	16.2	7.8	7.8	1.6
5	20	15.	9.	9.	1.2
6	25	14.	10.	10.	1.

tion. This made it practically impossible to determine the true induction factor with any degree of accuracy. The difficulty involved may be understood by the fact that at such high acid and tartrate concentrations the direct or voluntary oxidation of the tartrate rather than its induced oxidation became the predominant and controlling factor. A series of runs was tried in which an attempt was made to show how the corrected induction factor varied with increasing sodium tartrate concentration. The results obtained were as shown in Table XIII.

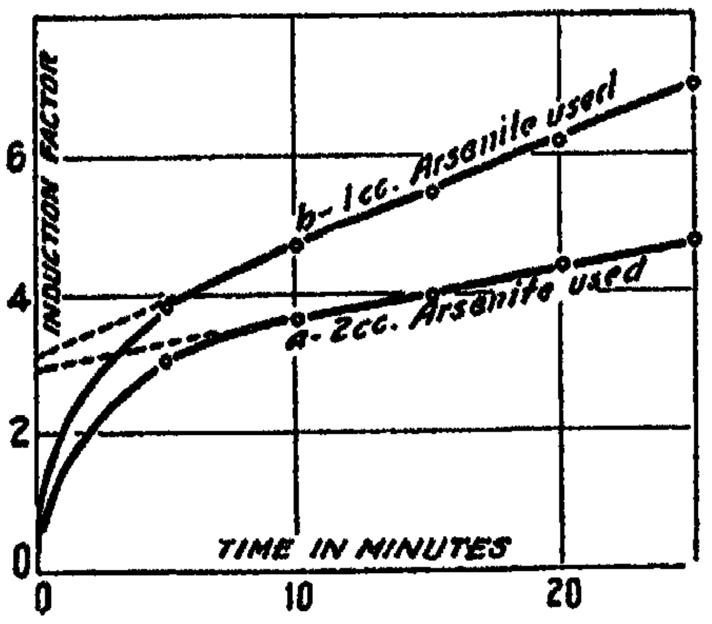

Fig. 11, Pt. 1 (a & b)

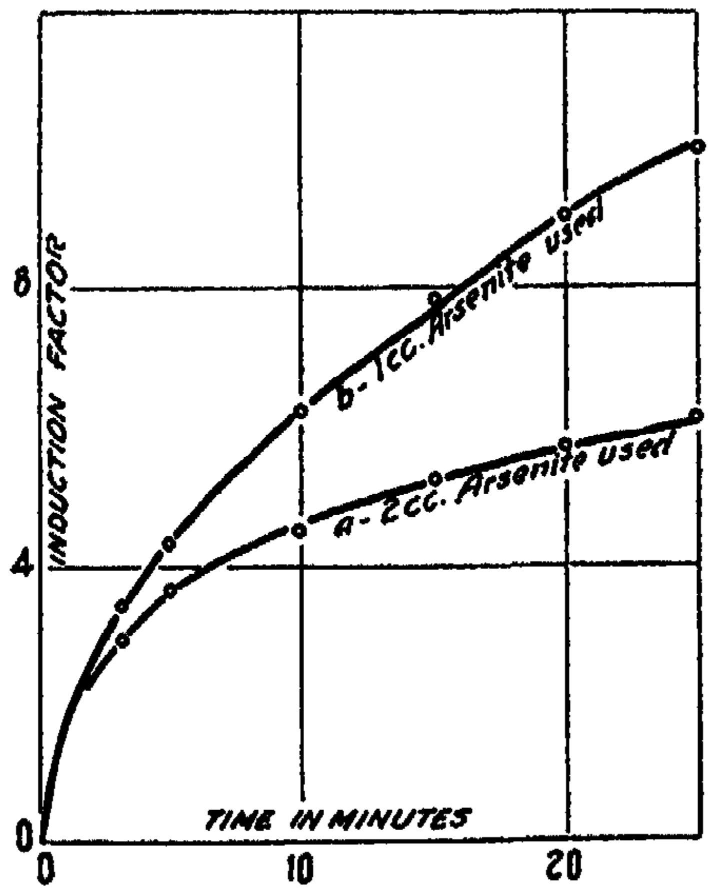

Fig. 11, Pt. 2 (a & b)

Considering these results as shown by Table XIII and Fig. 12 it seemed quite probable that at sufficiently high tartrate concentrations that the corrected induction factor would be greater than 3, yet as to just what its limited value would be, one could hardly say. With increasing sodium tartrate and sulphuric acid concentrations the rate of oxidation of the tartrate became faster and faster. This necessitated a continual reduction in the time allowed for the reaction to occur and as a result the correction to be applied for direct or voluntary oxidation became less and less accurate.

Since the true limited induction factor could not be determined with any degree of certainty using permanganate instead of dichromate as the oxidizing agent, the question as to whether the mechanism of the reaction envolved the formation of a complex between the tartrate and the arsenite or the formation of lower stages of the oxidizing agent remained unanswered. Further information in regard to this was obtained however by the determinations of the solubility of arsenious oxide in acid sodium tartrate solutions.

TABLE XIII

No.	Reaction Mixture	Corrected I.F. obtained
1.	10 cc .4N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc M/20 $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	1.55
2.	10 cc .4N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc M/10 $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	1.7
3.	10 cc .4N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc M/5 $Na_2C_4H_4O_6$ 2 cc N/100 As_2O_3	2.1
4.	10 cc .5N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc 4/10 M $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	2.7
5.	10 cc .6N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc M/2 $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	3.
6.	10 cc .8N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc 8/10 M $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	?
7.	10 cc N H_2SO_4; 25 cc N/100 $KMnO_4$; 5 cc M $Na_2C_4H_4O_6$; 2 cc N/100 As_2O_3	?

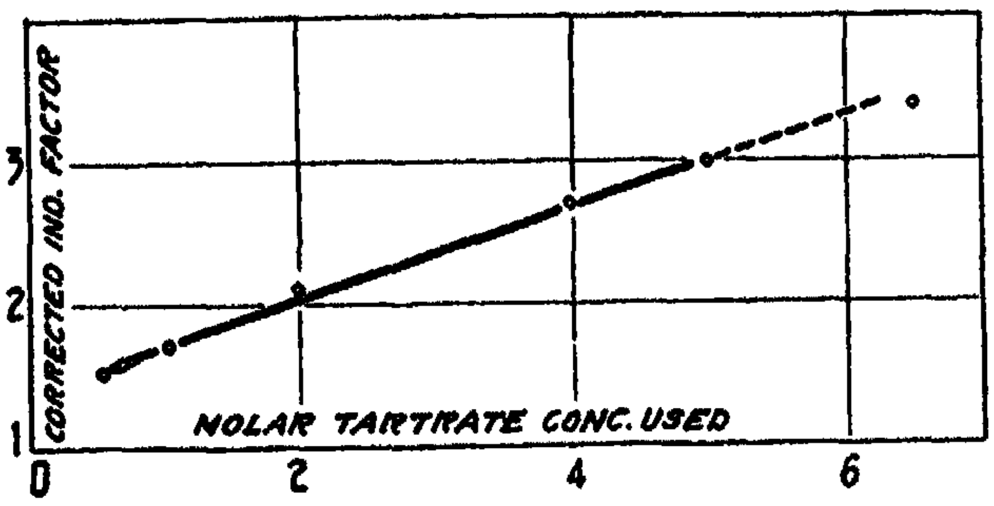

FIG. 12

Solubility of Arsenious Oxide in Sodium Tartrate and Tartaric Acid

As a further test of the possibility of the formation of a complex between arsenite and tartrate it was decided to determine the solubility of arsenious oxide in solutions of sodium tartrate made acid with tartaric acid. Kahlbaum's crystalline arsenious oxide (for analysis) was used for this determination. Solutions of Merck's sodium tartrate and tartaric acid were made up as indicated in the table, to which an excess arsenious oxide was added. The mixture was then placed in a shaker until a saturated solution was obtained. The saturation point was determined by taking out samples at various intervals and titrating with 0.2 normal iodine solution in an excess of sodium bicarbonate, this being repeated until constant results were obtained. This method of analysis was checked by a few determinations of the arsenious oxide in the form of As_2S_3 and was found to be satisfactory.

The pH of the various solutions was determined with indicators using buffer solutions before and after saturation with As_2O_3. The pH as determined before saturation was checked by means of a hydrogen electrode.[1] Such checks however could not be obtained after saturation due to the poisoning of the electrode by the arsenic present.

Table XIV

Temp. 22°C (Room).

No.	Pts. $Na_2C_4H_4O_6$	Pts. $H_2C_4H_4O_6$	pH	pH (after saturation)	Solubility of As_2O_3 in gms. per 100 cc.
1	700 M/5	.5 M/5	6.95	4.8	2.276
2	50 M/10	50 M/20	3.4	3.	2.58
3	50 M/5	50 M/10	3.34	2.9	3.35
4	0	100 M/10	2.08	2.08	2.05
5	0	100 M/20	2.3	2.3	2.03
6	Solubility of As_2O_3 in H_2O as determined				2.08

These results showed that arsenious oxide was less soluble in tartaric acid solutions than in water. In sodium tartrate solutions made acid with tartaric acid however, the solubility was found to be more than in water and to increase with the amount of tartaric acid added or with the hydrogen ion concentration of the solution. Further, on dissolving As_2O_3 in acid sodium tartrate solution the pH was decreased.

The only plausible explanation of this phenomenon appeared to be the formation of a complex between the arsenious acid and the undissociated sodium tartrate. This would explain why the solubility increased with increased acidity, as the amount of undissociated sodium tartrate would show a corresponding increase due to common ion effect. Further, the formation of such a complex would serve to remove tartrate ions from the solution, as more undissociated sodium tartrate would have to be formed in order to maintain equilibrium conditions. Tartaric acid would then supply tartrate ions to the solution by further dissociation and the corresponding hydrogen ions liberated would cause the observed decrease in the pH of the solution.

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[1] Through the kindness of Mr. L. L. Larson of this department.

Discussion

Consideration of the above facts, the limited induction factor of 4 as obtained using chromic acid as the actor, the possibility of the same induction factor using permanganic acid instead of chromic acid if correction could be made for voluntary oxidation of the tartrate in the more concentrated solutions, the maximum induction factor obtained with increasing acidity in both reactions studied and the increased solubility of As_2O_3 in sodium tartrate made acid with tartaric acid, showed the distinct probability that the mechanism of the reaction involved the formation of a complex between the inductor and acceptor as suspected by Schilow and that the reaction came under case 4 of the theory as presented. It must however be recognized that the possibility of the formation of a lower stage of the actor, case 2, has not been disproved and that both may occur simultaneously in the reaction.

The reaction studied has not resulted in a beautiful confirmation of the the theory presented because it proved to be much more complicated than could be expected from the data already published on the subject due to the fact that a reaction actually did occur between the actor and the acceptor and in addition to that was autocatalytic in nature. Nevertheless the advantage of the theory has been shown by the fact that it has led to a correction in the induction factor as previously obtained by Schilow and to a more complete understanding of the reaction studied than could have been obtained otherwise. The true test of the theory will come when several induced reactions have been studied which permit equilibrium conditions to be reached before analysis, provided such induced reactions actually do exist.

Summary

The results obtained in this investigation may be summarized as follows:

1. A review of the various theories of induced reactions has been given.

2. A new and better theory for studying reactions as developed by Professor W. D. Bancroft has been presented.

3. The induced reaction, chromic acid, arsenious acid and tartaric acid has been studied.

(a). A reaction was found to occur between chromic acid and tartaric acid which was autocatalytic in nature.

(b). The extent and speed of the direct oxidation of sodium tartrate has been shown to be dependent on temperature, time, acid concentration and strength of the oxidizing agent.

(c). The limited induction factor for this reaction after making proper correction for the voluntary oxidation of the tartrate by the chromic acid was found to be 4 instead of 2.8 as determined by Schilow.

(4). The mechanism of the above reaction, considering 4 as the induction factor, has been explained according to case 2 of the theory, namely thru the formation of Cr_2O_5 as the lower stage of the actor. As stated however, it may be equally as well explained according to case 4, or thru the formation of a complex between the inductor and acceptor.

(5). Experiments on the induced reaction, permanganic acid, arsenious acid, and tartaric acid gave an induction factor which increased with the concentration of the tartrate and acid present in the solution and whose true limited value could not be determined above 3 because of the pronounced voluntary oxidation of the tartrate by the permanganate in the more concentrated solutions.

(6). Arsenious oxide was found to be more soluble in sodium tartrate made acid with tartaric acid than in water which was believed to indicate the formation of a complex between the arsenious acid and the undissociated sodium tartrate.

(7). In the final analysis the mechanism of the reaction studied was believed to involve the formation of a complex between the inductor and acceptor altho the simultaneous formation of a lower stage of the actor could not be considered as an impossibility.

Acknowledgment

This investigation was undertaken at the suggestion and under the supervision of Professor W. D. Bancroft to whom the writer shall always be grateful for his good counsel and able guidance during the course of this research.

Cornell University,
June, 1927.

NEW BOOKS

Introduction to Modern Physics. *By F. K. Richtmyer. 22 × 16 cm; pp. xvi + 596. New York and London: McGraw-Hill Company, 1928. Price: $5.00.* "The purpose of this book is, frankly, pedagogical. The author has attempted to present such a discussion of the origin, development, and present status of *some* of the more important concepts of physics, *classical as well as modern*, as will give to the student a correct perspective of the growth and present trend of physics as a whole. Such a perspective is a necessary basis—so the author at least believes—for a more intensive study of any of the various subdivisions of the subject. While for the student whose interests are cultural, or who is to enter any of the professions directly or indirectly related to physics, such as engineering, chemistry, astronomy, or mathematics, an account of modern physics which gives the *origin* of current theories is likely to be quite as interesting and valuable as is a categorical statement of the theories themselves. Indeed, in *all* branches of human knowledge the "why" is an absolutely indispensable accompaniment of the "what." "Why?" is the proverbial question of childhood. "Why?" inquires the *thoughtful* (!) student in classroom or lecture hall. "Why?" demands the venerable scientist when listening to an exposition of views held by a colleague. Accordingly, if this book seems to lay somewhat greater emphasis on matters which are frequently regarded as historical, or, if here and there a classical experiment is described in greater detail than is customary, it is with a desire to recognize the importance of why," p. VII.

The first three chapters are devoted to a historical sketch: earliest times to 1550 A.D.; the rise of the experimental method, 1550-1800 A.D.; the rise of classical physics, 1800-1890 A.D. The fourth chapter deals with the electromagnetic theory of light, the fifth with some theorems concerning moving charges, and the photoelectric effect. After this comes a chapter on the origin of the quantum theory, followed by one on the quantum theory of specific heats. The remaining five chapters are entitled: series relations in line spectra; the nuclear atom and the origin of spectral lines; the arrangement of electrons in atoms; X-rays; the nucleus.

"If a sodium surface be illuminated by a tungsten lamp, the intensity of illumination being 0.1 meter-candle, it should require several hundred *days* of continuous illumination before a photoelectric current starts to flow, *if we assume:*

1. That the photoelectron comes from the atom;
2. That the atom absorbs from the incident light the energy required to expel the electron;
3. That each atom in the surface layers of the photoactive material absorbs only its own proportionate quota of energy—as seems required by the wave theory of light.

But there has never been observed any time lag between the beginning of illumination and the starting of the photoelectric current. Indeed, some recent measurements show that, if there be such a time lag, it is less than three billionths of a second. Clearly one (or more) of these three assumptions just stated must be wrong, since the experimental facts and the numerical data on the basis of which the computation is made seem to be well founded.

"The classical electromagnetic theory of light, therefore, not only gives us no clue as to the mechanism by which photoelectric emission occurs; but, also, it seems to be in direct conflict with well-established experimental facts, which facts point unmistakably to some kind of discontinuity or structure to what, heretofore, we have called a wave front.

"If we could discuss the phenomenon of interference of light and the deductions therefrom, both experimental and theoretical, and if, with Newton, we could return to the corpuscular theory, the difficulties raised in the preceding section could be easily explained, at least qualitatively. Thus on the corpuscular theory, we might regard a beam of light as a 'rain' of corpuscles of energy. When such a 'shower' of light falls on the sodium surface, only here and there an atom is being struck by a corpuscle at any given instant. If, now, we assume (1) that each corpuscle, or 'quantum' in modern terms, possesses energy

$h\nu$ and (2) that by some unknown process, a 'collision' between a quantum and an atom may, under suitable circumstances likewise quite unknown, result in the absorption of the whole quantum by the atom and the subsequent emission of the photoelectron with the initial energy $h\nu$, we can, at once, explain why only one atom in many millions expels an electron in any particular second and also, why there is no time lag in the photoelectric process," p. 173.

"The difficulties with such a radial theory of light are many. For example, if we regard light, incident onto a surface, as a 'shower' of corpuscles or quanta of energy, what can possibly be the meaning of *frequency* in connection with such a phenomenon? There is nothing periodic about a falling rain drop, unless we think of a drop as in revolution about an axis through its center of gravity as it falls, the speed of this angular rotation determining the frequency, and the distance fallen during one revolution being a 'wave length.' Nevertheless, frequency plays a very fundamental role in determining the energy $h\nu$ of the quantum. It should be pointed out, however, parenthetically, that we do not measure *directly* the frequency of a light ray. We *measure* (1) the velocity c of the light and (2) its wave length (λ) *on the assumption that light is a wave motion*, and then we *compute* the frequency ν by the equation $c = \lambda\nu$. *We have to rely on the wave theory of light to give us the energy value* $h\nu$ *of a quantum.*

"And there still remains the phenomenon of interference, which, since its discovery by Young in 1802, has defied explanation on any other basis than by assuming light to be a wave motion. However, the experimental facts of photoelectricity are equally as cogent as the phenomenon of interference, and *they cannot be explained on the basis of the present wave theory* of light. Here, then, is the most perplexing question of modern physics, a question which physicists have been trying to answer for 2½ centuries: Is light undulatory or corpuscular? In spite of the vast amount of data bearing on the subject, we, today, are apparently no more able to give a categorical answer to the question than were Huyghens and Newton," p. 174.

"The universally accepted scale of temperature is the Kelvin scale. It cannot be utilized *directly;* but is approximated with sufficient accuracy for experiment by a gas thermometer (hydrogen or, for higher temperatures, nitrogen). Due to obvious limitations, it is impossible to use gas thermometers above temperatures of 1300° or 1400°C. It is therefore impossible to extend the Kelvin scale, *by means of the gas thermometer*, above this temperature. The several radiation laws—Stefan's and others—are checked experimentally up to 1300° or 1400°C. by use of the gas thermometer. Beyond these temperatures, *the laws themselves are used to establish a temperature scale.* This procedure is perfectly logical, particularly in the case of Stefan's law, since that law itself is derived by use of the Carnot's cycle, which forms the basis of the Kelvin scale. In other words, excepting as one method may be superior to another experimentally, it should be a matter of indifference, in realizing the Kelvin scale, whether we use a gas thermometer (making corrections for the actual gas used so as to make the measurements conform to a *perfect* gas scale, which, in turn, is identical with the Kelvin scale) or whether we use a radiation law, such as Stefan's which is based upon Carnot's cycle, and which likewise, should, provide a satisfactory means of realizing the Kelvin scale," p. 202.

"It is worth commenting on the fact that Planck's revolutionary assumption $\epsilon = h\nu$ was not based upon logical reasoning following the ordinary lines of classical physics. Quite the contrary: *the assumption was an attempt, entirely empirical, to bring the deductions of classical physics into harmony with experiment.* And the attempt was most astonishingly successful," p. 240.

"Strictly speaking, the Ångström is not defined from the meter as a *primary* standard of length. Michelson and Benoist in 1895 and, later (1907), Fabry, Perot and Benoist measured the wave length of the red cadmium line in terms of the standard meter. The two measurements were almost exactly in agreement; the wave length according to the latter measurement being 6438.4696 Ångströms. The International Union for Solar Research, in 1907, adopted this value of the wave length of the red cadmium line as the *primary* standard of wave length, on the basis of which all the other wave lengths were to be expressed. Formally, this amounts to a new definition of the Ångström in terms of the wave length of the cadmium line such that this wave length is *exactly* 6438.4696 Ångströms. Other wave lengths are expressed in terms of the Ångström so defined," p. 290.

"The classical theory, however, fails completely to account for the *abnormal* Zeeman effect, in spite of the fact that *the success of classical theory in* explaining the normal Zeeman effect and in deriving therefrom *the correct value of* (e/m *was one of the very strong supports for the existence of the electron*," p. 322.

"The picture of the atom and its vibrating mechanism, which one has in mind in considering the effect of temperature and pressure on the width of the spectrum lines, *is more or less definitely based upon the classical concept of the emission of radiation in long wave trains.* Indeed, we might regard the explanation of these comparatively minute effects *as a final triumph of classical theory.* These effects can be explained by the quantum theory, but the quantum theory suggests *no picture* of the radiating mechanism involved.

"In this chapter, we have presented a brief outline of some of the experimental facts connected with the characteristic line spectra of the atoms and molecules. We have limited the discussion to the visible and near-visible region of the spectrum, omitting, for example, all reference to X-ray spectra, since the latter can best be presented in connection with a consecutive discussion of X-ray phenomena. We have seen that the data are very complex: that a given atom may emit hundreds or even thousands of lines, each line involving a perfectly definite, sharply defined, frequency. We have seen that the relation between the frequencies of the various lines in the spectrum of a given element are such as to preclude the possibility of their arising from a fundamental frequency and its overtones. Classical physics could picture no atomic mechanism composed of electrons and positive charges and capable of vibrating in so many different modes. In characteristic line spectra, as in temperature radiation, the quantum theory succeeded, when the classical theory failed," p. 328.

"It should be emphasized that we should not take this picture of the atom with its several electrons revolving in the various 'privileged' orbits too seriously, at least so far as concerns *the actual physical* makeup of an atom. The concept of orbits and of the 'dropping of electrons from one orbit to another' is of value largely in helping us to keep in mind the *observed* phenomena and in suggesting other previously unknown phenomena which, in turn, suggest new experiments. It is probable that the picture of an atom with a planetary system is as far from the real architecture of the atom as are 'lines of force' from the actual structure of the magnetic field. We find the concept of lines of force very useful in helping us to visualize certain phenomena. We compute electromotive forces by ascertaining the number of lines cut per second. Yet we know that, physically, there are no such lines in a magnetic field as we find it convenient to visualize. We do know, however, that *irrespective of any concrete picture of its structure, a magnetic field involves energy,* the amount of which per unit volume at any point we can compute by dividing a certain quantity H^2, characteristic of the field at the particular point, by 8π.

"In a similar way, the concept of orbits, electron transfers, and the like is a very concrete and useful geometrical 'picture' to help us keep in mind the various *states* of the atom. But whether the *picture* be correct or not, we are reasonably sure that the *energy* associated with these various stationary states is *real*. Sometimes it is more convenient to speak in terms of orbits; at other times, the more general phrase 'energy corresponding to a given state' will be more appropriate. We should always keep in mind, however, that the latter phraseology is physically justified; the former is quite artificial," p. 384.

"The Rutherford-Bohr atom *model* was built out of raw material which grew in the field of physics. The atom *itself*, originally a child of Chemistry, was soon adopted by physics and has long claimed this joint parentage. In all of our theories and theorizing, we must not fail to distinguish between the *real atom* and the *atom model*. The ultimate atom model—*if such perfection be ever reached*—must explain and agree with the facts of chemistry, which facts are just as cogent as are the facts of physics. The task of constructing an *atom model* which shall do all the things that *atoms* are made to do by both chemists and physicists was (and is!) gigantic. A model, built and trained to act as marionette for a physicist, could not be expected to perform well for the chemist.

"Out of the material furnished by chemistry have been built various atom models, which, in the main, go by the generic name of *static* atom models, as contrasted with a model of the Rutherford-Bohr type, which is a *dynamic* model. The origin of the two terms is significant. The dynamic model has been constructed by the physicist largely from information acquired in watching atoms *in action* or, at least, in watching the results of their activity, such as the emission of radiation, characteristic or black body, or the scattering of α particles, and the like. It is natural, therefore, that the physicist should picture an atom as full of *moving* mechanisms. His one static atom, the Thomson model, proved inadequate. The chemist, on the other hand, is somewhat more concerned with the atom at rest. He weighs it in finding what combinations it makes with other atoms; he observes it apparently at rest in crystals, except for possible thermal agitation; he thinks of it as occupying a definite position as one of the constituent atoms of various complex molecules, being held in place by certain interatomic forces, perhaps of electrostatic origin. It was difficult to see how a thing so full of whirling mechanisms as the physicist pictured the atom to be could keep as quiet as the chemist found it when *he* looked at it. Hence, the static atom," p. 412.

"There has been much criticism of the 'static' atom model. Thus, one eminent writer states: "It is true that if the eleven postulates, on which Langmuir's theory is founded, are granted, and a certain freedom of interpretation be allowed, a great body of chemical observation is covered by this theory, but it must be observed that the postulates have very much *ad hoc* character, often paying little attention to any established laws of electromagnetism." As if Bohr's postulates or Planck's quantum hypothesis paid any attention to the 'previously established laws of electromagnetism'! It is the essence of the whole quantum theory that *ad hoc* assumptions are made, *ad libitum*, where such assumptions serve a useful purpose. Of course, the fewer such assumptions the better. But, logically, we may as well make a dozen assumptions contravening classical theory, as one. If atom models growing out of the concept of the orbital motions of electrons, *i.e.*, the so-called 'dynamic' atom models, *have* been more successful than static atom models, it is because the former have been more prolific in explaining and interpreting physical phenomena, rather than because of any superiority in fundamental tenets. The great number of *qualitative* deductions from static atom models, deductions in agreement with chemically observed facts, is very suggestive. But *the computation of spectral frequencies, even for one atom, from fundamental constants of nature is a quantitative achievement that is all but convincing*," p. 416.

"At the beginning of the century, there was a vague impression that the atom consists of electrical charges. We saw that Thomson's picture gave way, before experimental evidence, to the Rutherford-Bohr type of atom in which the *nucleus* was thought of as a *point* charge, just as the atom itself in the early chemical theories played the part of a point mass. Now, the nucleus itself succumbs to analysis, protons and electrons playing the part of *point* charges in the proposed structure. Will these, in their turn, yield to analysis and be assigned a structure? Or have we reached the end of the series?

"Physics of today seems quite secure, in spite of the chasm between classical theory and quantum theory, but perhaps some day some Copernicus will appear who will completely overturn our present exceedingly complex structure of physical theories and concepts and show us a beautiful simplicity in the laws of nature. If physics continues to grow at the present geometrically increasing rate, the physicist of a half-century hence will welcome such a revolution with open arms," p. 564.

Wilder D. Bancroft

The General Properties of Matter. *By F. H. Newman and V. H. L. Searle. 22 × 14 cm; pp. 388. New York: The Macmillan Company, 1929. Price: $5.50.* In the preface the authors say: "The present book, which is intended primarily for the physicist, embodies the results of much practical experience in the teaching of physics, and it is an attempt to present a fairly complete survey of the fundamental properties of matter, with the special aim of developing those branches of the subject, such as surface tension, osmosis, and viscosity which verge towards chemistry, and hydrodynamics and vibrations which are of importance and interest more particularly to the mathematician and engineer. By this development, and throughout the book, the aim has been to emphasize the essential unity of scientific knowledge," p. 5.

The chapters are entitled: general principles; acceleration of gravity; gravitation; gyroscopic motion; elasticity; surface tension; viscosity; the kinetic theory of matter; Fourier's theorem; osmosis and diffusion; dynamical basis—including vibrations; equations of motion; wave motion in liquids; units and dimensions.

Newton's law of gravitation "has been regarded as the most perfect generalisation of experience in the whole of Physics, because, on the one hand, its range is so wide and, on the other, there is such a vast amount of confirmatory evidence—the divergences, indeed, being so few that until recently it was thought that they were due to undiscovered perturbing influences rather than to a want of exactness in the law. It is now realised, however, that serious objections may be raised to the above enunciation as a complete description of gravitational force, although these cannot, of course, destroy the harmony between the overwhelming majority of experimental facts and the predictions arising from the Newtonian formula. We shall later discuss the evidence in favour of this law and review briefly the considerations for the modern view introduced by Einstein," p. 59.

"Before the outstanding discrepancies are discussed, however, there are two difficulties inherent in Newton's enunciation which are the chief reasons for criticism. In the first place, the mass of a body varies with its velocity and we are left in considerable doubt as to what value is the correct one for insertion in the formula. Secondly, distance is not as fundamentally simple as it appears to be, since the measurement assigned to a distance depends upon the circumstances of the observer making the measurement. It is not intended here to present a full description of Einstein's relativity theory: but reference to the Michelson-Morley experiment will indicate that the numerical value assigned to the distance between two points varies according to the system of space co-ordinates chosen, *i.e.* to the observer making the experiment. The negative result of this experiment is usually explained by the Fitzgerald contraction of bodies in their line of motion. There is therefore a similar ambiguity about the remaining term in the Newtonian Law. These two differences are, of course, small; but it was by taking them into account—an incidental consequence of the theory of relativity—that the outstanding deviations from the Newtonian Law were explained.

"The two main differences between the predictions of the Newtonian and Einstein Laws of Gravitation refer to the motion of the perihelion of Mercury and the bending of a ray of light passing close to the sun.

"The differential equation to an orbit under the Einstein law is:

$$\frac{d^2u}{d\theta^2} + u = \frac{a}{h^2u^2} + 3a,$$

where $r = 1/u$ is the radius vector, θ the other polar co-ordinate referred to an origin at the centre of force a the acceleration towards the centre, and h is twice the value of the constant areal velocity of the radius vector. This differs from the equation under the Newtonian Law by the term $3a$ which measured the motion of the perihelion—or orbital point nearest to the sun—and gives the same value as that observed and which was previously unaccounted for.

"A ray of light has a mass which is appreciable by reason of its great velocity, and thus should be deflected when moving in a strong gravitational field. The deflections, and thus the apparent shift of the light source, may be calculated according to both laws. There is, at present, *no* possibility of making a test of this effect on a terrestrial scale owing to the extremely minute lateral displacement in a moderately long ray path; but conditions are favourable during a total solar eclipse when stars may be seen in a direction close to the edge of the sun. In these circumstances the apparent displacement is of the order of one second of arc which, with a long focal length telescope, is easily measured with accuracy. Einstein's theory predicts a movement double that given by Newton's Law, and experiment has shown again in this case that the former is verified as accurately as experimental errors permit," p. 76.

Gyroscopic motion is discussed without any reference to Sperry, whose name might at least have come in under applications. Instead, the authors say, p. 98: "The single track train, or mono-rail, of Brennan is stabilised by gyrostats, while a similar use to stabilise vessels was suggested by Schlick."

The authors consider that Jaeger's second method when used with the equation given by Schrodinger and by Verschaffelt is probably the most accurate one for determining surface tensions, p. 157. Since the authors wish to use the Gibbs equation for the change of concentration in the surface film of a solution, they introduce the phase rule in the midst of the chapter on surface tension, p. 176, where it certainly does not belong, and without stating that the equation for the degrees of freedom does not apply in cases where surface tension phenomena are important. Hardy's work on lubrication is apparently not brought beyond 1920, p. 218.

The authors make no distinction, p. 273, between ultra-filters and semipermeable membranes. They are a little vague as to what was done by Pfeffer and what by van't Hoff, p. 275. They evidently have no idea what the exact equation for the osmotic pressure is, p. 279. On the same page, p. 275, they have V the volume of a solution containing one gram-molecule [of the solute?] and the molecular volume of the solvent under standard pressure conditions. Both statements cannot be right and, actually, neither is. It would simplify matters if physicists who write on topics in physical chemistry, would read up the subject.

Wilder D. Bancroft

Photochemische Versuchstehnik. *By J. Plotnikow. Second enlarged edition. 23 × 17 cm; pp. xvi + 457. Leipzig: Akademische Verlagsgesellschaft, 1928. Price: 20 marks; bound 21.60 marks.* Some tables have been added and some new pieces of apparatus have been described; but otherwise the edition has not been changed much. A complete revision is promised for the third edition; but no date is set. The subject is presented under five heads: sources of light; thermostats for photochemical work; optical measuring instruments; photochemical lecture experiments; photochemical tables.

On page 230 the author says: "All photochemical reactions conform to three fundamental laws. The first is that only those rays which are absorbed by the substance in question can produce chemical action. The converse of this is not true, that every ray which is absorbed must cause chemical action. The second fundamental law is that the rate of a photochemical reaction changes proportionally to the absorbed quantity of light and not to the intensity of the light. According to the third law the light reactions differ essentially in their mechanism from the ordinary dark reactions and the properties of the photocatalytic reactions are the sum of the dark and the light reactions."

This paragraph will have to be changed a good deal in the next edition. There is no reference to depolarizers, in spite of the fact that Grotthuss formulated the theory of them over a century ago. The universal applicability of the second law is open to question. Since the action of light on a mixture of carbon monoxide and chlorine is the same in principle as the catalytic action of charcoal or the thermal effect of a temperature rise, the wording of the third law should be revised. There is nothing said at all as to the possibility of different wave-lengths producing different chemical reactions with any one organic compound.

According to the data of Berthelot and Gaudechon, p. 251, ultraviolet light converts acetaldehyde very largely into ethane, hydrogen, and carbon monoxide instead of into methane and carbon monoxide as one might have expected.

The author claims, p. 258, to be the first to have illuminated an audience with strong ultra-violet light (1926); but the public lectures of R. W. Wood go back of that.

Wilder D. Bancroft

An Introduction to Modern Organic Chemistry. *By L. A. Coles. 19 × 13 cm; pp. xv + 462. London: Longmans, Green and Co., 1929. Price: 7 shillings, 6 pence.* This book is intended to be a text-book, both theoretical and practical, for use in the upper forms of schools. It falls into four sections. The first is partly experimental, dealing with alcohol and acetic acid, and is partly devoted to the fundamental ideas and methods. The second and third are general accounts of the more usual aliphatic and aromatic compounds respectively; the descriptive matter is interspersed throughout with preparations. Finally the last chapter is a very compressed history of organic chemistry.

Some will think the book well adapted to its purpose; others, including the reviewer, are of the opinion that large masses of organic chemistry should not be taught in schools, and this book certainly goes fairly far; the isomerism of the oximes and the synthesis of alizarin and indigo appear. This is not the place for a discussion of policy; the matter is best left by saying that the book is of the type in which a large number of compounds are discussed very shortly.

The first part of the book is the best. It is original in its method of approaching the subject and has been written with care. The historical chapter at the end is a valiant attempt to achieve the impossible, for without wide reading and deep thinking it will always be impossible for a student brought up with clear ideas about atomic weights and valency to cast all that out of his mind and to appreciate the etherin theory and the theory of types.

The main part of the book, a short systematic account of organic acompunds calls for little comment. The reviewer is puzzled as to the word "Modern" in the title. The account follows the ordinary channels and where recent work might well be mentioned, nothing is said. The author should revise his section on the oximes of benzaldehyde; the facts are untrue as he states them, and the validity of the Hantzsch-Werner method of establishing their configurations, which he describes as obvious, has been in serious doubt, to put it mildly, for the last eight years. In the discussion of acetoacetic ester some mention of Knorr's simple experiments (1911) would be of much greater value than the account of Claisen's somewhat doubtful theory as to its formation. As a final example, the author, following tradition, settles the configurations of maleic and fumaric acids by an appeal to their oxidation to the tartaric acids, an argument which makes the reviewer's blood boil; for trans-addition to a double bond is at least as common as cis-addition, and one does not know which one has got until the configurations are known, so that the argument is a very poor way of arriving at the non-configurations. A phrase which needs modification is the definition of an electrolyte as a substance "which in solution renders the solvent capable of conducting electricity."

The preparations given in the book are, on the whole, very well done.

T. W. J. Taylor

Photo-electric Phenomena. *By Bernhard Gudden. 22 × 14 cm; pp. ix + 325. Berlin: Julius Springer, 1928. Price: 24 marks; bound 25.20 marks.* The book is not intended to be a text book for the student of photo-electric phenomena. It is essentially a record of experimental work, and little space is given to theoretical considerations. This book divides itself naturally into two parts, the first part, consisting of the first nine chapters, dealing with various aspects of the true photo-electric effect, i.e. the complete ejection of electrons from matter by radiation, often known as the 'external' photo-electric effect by German writers. In this part of the book much ground is covered and a special chapter is included dealing with the application of the effect to the measurement of light intensity by photo-electric cells. In the second part—the remaining seven chapters—the author is mainly concerned with the 'internal' photo-electric effect, i.e., the changes in conductivity which occur on illumination, due to some kind of 'loosening' of the electrons without their complete ejection. A large part of the author's well known work on this photo-electric conductivity effect in various crystals is here discussed, and a special chapter is devoted to the case of selenium and the selenium cell. Over 600 references are given, covering the period from 1914 to 1928. The book is a most valuable one and contains a considerable amount of information not given in the standard textbooks on 'Photo-electricity'. *F. C. Toy*

Bandenspektra und ihre Bedeutung für die Chemie. *By R. Mecke. 25 × 16 cm; pp. 87. Berlin: Gebrüder Borntraeger, 1929. Price: 7.60 marks.* In this little monograph of 87 pages Dr. Mecke has brought together a lot of very useful information about a rapidly developing subject. By his own researches in the field of band spectra Dr. Mecke is well qualified for his task, and the arrangement and presentation of the data are attractively made. The book does not include any advanced mathematical treatment but gives a clear and straightforward account which may be easily followed by anyone having no specialized knowledge of the subject. Successive parts of the book deal with the theory of band spectra and the structure of bands, and these are followed by an account of the application of the knowledge of band spectra to the relevant problems of physics and chemistry. Among the latter may be mentioned chemical valence, energy of molecular dissociation, the chemical constant, isotopy, and the specific heats of gases. Within the allotted space the author has compressed an excellent account of the type of work which has been done in these various departments of the subject. The monograph of course does not set out to present a detailed record of all this work which would indeed require many volumes. In its scope and treatment it is also very different from the Report on Molecular Spectra in Gases. This renders it the more valuable. We believe this little book will prove very valuable to those whose knowledge of the subject is elementary, and who desire an acquaintance with its developments and its important applications. Research workers and others will also find here several useful tables of molecular constants.

R. C. Johnson

Probability and its Engineering Uses. *By Thornton C. Fry, 23 × 16 cm; pp. xiv + 476 New York: D. Van Nostrand Company, 1928. Price: $7.50.* This book covers the ground of a course of lectures delivered at the Massachusetts Institute of Technology. The chapters are entitled: introduction; permutations and combinations; elementary principles of the theory of probability; probability and experiment—Bernoulli's theorem; probability and experiment—Bayes' theorem; distribution functions and continuous variables; averages; the distribution functions most frequently used in engineering; curve fitting; the theory of probability as applied to problems of congestion; fluctuation phenomena in physics.

The reviewer's training has been unfortunately so limited that the only portion of the book which appealed strongly to him was the opening quotation: "Coincidences, in general, are great stumbling-blocks in the way of that class of thinkers who have been educated to know nothing of the theory of probabilities; that theory to which the most glorious objects of human research are indebted for the most glorious of illustration."

Wilder D. Bancroft

ERRATA

In the paper on the "Flow of Clay Pastes through Narrow Tubes" by G. W. Scott Blair and E. M. Crowther: J. Phys. Chem., 33, 321 (1929), the following corrections should be made:—

P. 327 line 14, "a constant (a)" should read "a constant (X);"
P. 328 Table III, the heading of the fourth column should read "c(cmHg)";
P. 330 line 14, the second term of the equation should read "$+\pi R^2\epsilon\varphi(P\text{-}a)$."

Vol 33 N[illegible] No 11

INDUCED REACTIONS AND THE HIGHER OXIDES OF IRON

BY DANFORTH R. HALE

Introductory

The induced reactions in which ferrous iron is the inductor have caused much pother among investigators ever since 1858, when Schönbein[1] found that blood corpuscles and ferrous salts accelerate the decolorization of indigo blue by hydrogen peroxide. In the attempt to account for these reactions, no fewer than eleven intermediate compounds and radicals containing iron have been postulated, depending on the oxidizing agent and the acidity of the solution. A few of these have similar empirical formulae, but all are different in their assumed structure. The two classifications proposed—the one by Schilow (1903) based on specificity of reagent and the other by Miller (1907) based on effect of reagent on reaction velocity—are unsatisfactory, and seem to have no pragmatic value. Aside from its purely intrinsic interest, the problem is important as bearing on such questions as the passivity of iron, the anomalous break in potentiometric titration curves involving ferrous iron and an oxidizing agent, and oxidation in biological chemistry.

The purpose of the research with which this thesis deals is to investigate the more probable of the postulated intermediate compounds, to sift the evidence for these, and if possible to develop a mechanism for the reaction which will explain the observed phenomena.

Perhaps the classic example of an induced reaction is the oxidation of an arsenite solution by means of air in the presence of sodium sulphite. Friedrich Mohr called attention to this arsenite reaction in 1855, but to this day its mechanism is obscure. As this is the induced reaction most often referred to, and one that has the dignity of age, it may well serve here to illustrate the significance of the term. Speaking of the stability of an alkaline tenth-normal arsenite solution in contact with air, Mohr[2] said:

"When sodium arsenite is allowed to stand in an open vessel with a little sodium sulphite added, it is not long before arsenic acid is also found in the solution. While the sodium sulphite is undergoing oxidation the arsenious acid is infected with the oxidation process. I placed in a flask some of the solution that I had already kept ten months without change in strength, and dropped a single crystal of sodium sulphite therein. After two weeks the solution gave a red-brown precipitate with a silver solution, and with magnesium mixture gave in large amounts the characteristic, coarsely-grained, crystalline precipitate of magnesium-ammonium arsenate." It will be remembered that sodium sulphite solution is rapidly oxidized to sulphate if allowed to stand in contact with air.

The two reactions may be written separately thus:

$$O_2 + 2Na_2SO_3 = 2Na_2SO_4$$
$$O_2 + 2Na_3AsO_3 = 2Na_3AsO_4$$

where the first is the rapid reaction and the second is the reaction which apparently does not occur spontaneously at all, but which occurs readily enough if the other reaction is taking place in the same solution.

F. Kessler[5] in 1863 developed the terminology which will be used in the sequel: The rapid reaction, the oxidation of the sulphite is the *primary reaction*; the slow or nil reaction, the oxidation of the arsenite, is the *secondary reaction*, which is said to be *induced* by the occurrence of the former in the same solution. The oxygen, logically enough, is the *actor*; the arsenite is the *acceptor*; and the sulphite, the actual accelerating agent, is the *inductor*. The proportion in which the actor divides itself between the acceptor and the inductor is called the *induction factor*, the relative amounts being measured not in gram molecules but in gram equivalents.

The story of the reactions induced by ferrous iron is but a chapter in the history of the induced reaction, which, first recognized about 1855, has been the subject of much investigation and of various theories and attempts at classification, resulting, however, in so small a body of definite knowledge and proven theory that the term is rarely found to-day in the indices of chemistry textbooks. Induced reactions have been likewise designated as "coupled" (W. Ostwald)[6] and "sympathetic" (J. W. Mellor)[7] reactions; but these terms are quite as rarely met with. Wagner[8] calls the phenomenon "pseudocatalysis." Dhar's translation[9] of Ostwald's term is "catalysis by transvection."

C. F. Schönbein[10] was probably the first experimenter to speculate on the actual mechanism of induced reactions. In 1858 he showed that ozone is formed when phosphorus is oxidized by oxygen, and that when benzaldehyde or turpentine is oxidized, indigo in the same solution is simultaneously oxidized to colorless isatin. He demonstrated that the oxygen which is consumed is divided equally between the two substances oxidized, and this has been verified by van't Hoff[11], Jorissen[12], Engler[13], and others for several organic and inorganic substances. Schönbein's explanation[14] (1860) was that during the oxidation an oxygen molecule breaks up into two atoms of opposite charges, and that these naturally would tend to oxidize different substances.[15, 16]

Engler[13] calls this phenomenon "autoxidation" or "auto-oxidation"—actually a misnomer, since, although the reaction is an oxidation, neither of the substances oxidized has the power of oxidizing itself as, for instance, potassium hydrochlorite has. The terms, however, are in the literature and the dictionaries, and must be reckoned with. At any rate the phenomenon is an induced reaction. In the phosphorus experiment the oxidation of the phosphorus is rapid; the oxidation of gaseous oxygen to ozone is relatively extremely slow or nil, but is greatly accelerated while the phosphorus oxidation is in progress.

Moritz Traube[17] in 1882 expressed disagreement with the positive and negative oxygen atom theory. He showed that many oxidations, if occurring in the presence of water, induce the formation of hydrogen peroxide in small quantities. An instance of this is the reaction of zinc and oxygen, in which, by Kessler's nomenclature, the actual oxidation of the zinc may be called the primary reaction. Then zinc is the inductor and water is the acceptor of the induced reaction. Traube suggests that molecular oxygen adds itself to the hydrogen of a water molecule, forcing out the oxygen atom, which then combines with the zinc. If this is the correct explanation, then the oxygen first unites with the acceptor.

In 1897 A. Bach[18] and in 1902 Wilhelm Manchot[19] stated the view that the substance undergoing rapid oxidation, the inductor now, unites with oxygen to form a peroxide. It is this theory, particularly for those reactions in which ferrous iron serves as inductor, which has received most attention and which is supported, for certain cases, in the present thesis. Manchot, of all the many investigators in this field, has probably done the soundest, practical and theoretical, work on induced reactions. The reactions he studied and the compounds he postulated have served as the basis for a number of researches, including this one. His first paper[20] appeared in 1899; his latest[21] in 1927.

R. Luther and N. Schilow[22] in 1903 developed a general classification of induced reactions which was based on the specific action of inductor, actor, acceptor, and combinations of any two. Thus the induced reaction involving ferrous iron comes under Class A—inductor specific—for if suitable other compounds are used for the actor and acceptor the reaction is still induced, but if another metal is used in place of iron the reaction will probably not go at all. This system gave six classes, but it is very one-sided, for all reactions involving ferrous iron as the inductor côme under Class A, and the eight known reactions in which sulphur dioxide is inductor are distributed among the other five classes. This is not necessarily an objection to the classification, because the reactions might perhaps be distributed that way. The real objection is that Luther's classification is quite arbitrary.

W. Lash Miller[23] of Toronto wrote in 1907 a paper which was the culmination of several investigations carried on under his direction on the subject of reaction velocity in oxidation-reduction processes. These are published in the Journal of Physical Chemistry beginning in 1903. He himself puts forward no theory; but, in an early paper by Miss Clara Benson,[24] a complicated theory for the iron reaction was advanced which involves the assumption of a "ferroiodion," FeI^+, a device which serves to account for certain peculiar effects occurring in the reaction velocities. The essence of her findings is that in the absence of iodides the rate of oxidation of ferrous iron by chromic acid is proportional to the square of the acid concentration and to the square of the ferrous salt concentration, whereas in the presence of iodides this rate of oxidation is proportional to the third or fourth power of the acid concentration, and to the first power of the ferrous salt concentration. This result seems to throw doubt on Manchot's primary reaction, the oxidation of ferrous iron to a peroxide, since this primary reaction ought to take place in the same manner whether iodide is present or not. By assuming the temporary existence of the ferroiodion, the change in velocity when iodide is added becomes plausible, but Miss Benson does not attempt to explain the particular exponents that she found. These reaction velocity measurements will be mentioned again later.

Miller classified induced reactions using as a basis the effect of the reactants on the reaction velocities. In Class I the presence and concentration of acceptor has no effect on the rate at which the inductor is acted upon. In Class II the rate of change of the actor is independent of the presence and concentration of the acceptor; and in Class III the addition of acceptor changes the effect of the reagents on the rate at which the inductor is destroyed.

Some time in 1923, Wilder D. Bancroft[25] outlined a classification of induced reactions based on the possible mechanisms through which they might occur. This seemed more logical than a classification founded on arbitrary properties of the reactions or on reaction velocity. To quote his words: "Let A be an oxidizing agent (actor), which will not react with a reducing agent C (acceptor), but which reacts with a reducing agent B (inductor) and with C in presence of B." Five types of induced reactions may then be distinguished:

1. B may catalyze the reaction between A and C.
2. C may react with a low stage of A.
3. C may react with a high stage of B.
4. B and C may form a complex.
5. Combinations of the above may occur.

It should be noted that two varieties of catalysis are admitted to the class of induced reactions by this classification. The inductor is not usually a catalyst, for it disobeys one of the criteria: no permanent chemical transformation. The first type of induced reactions, however, are those in which the inductor acts in a truly catalytic manner in bringing about a reaction between actor and acceptor, but in which a molecule of inductor, having catalyzed the reaction of any actor and acceptor in its sphere of influence, is transformed by the actor into a substance not possessing the catalytic activity.

A second form of catalysis belongs under Type three. As an example of this, furfural is not oxidized in the presence of sodium chlorate alone, but is rapidly oxidized if a little vanadium pentoxide is added.[6] Vanadium pentoxide alone oxidizes furfural and shows the following changes of color: V_2O_5 (yellow), V_2O_4 (blue), V_2O_3 (green), which are immediately reversed when a crystal of chlorate is added. Assuming the use of an excess of chlorate, the pentoxide is a catalyst and it obeys the criterion of not undergoing permanent change. Yet the reaction is an induced reaction, for the slow furfural-chlorate reaction is accelerated in the presence of the rapid furfural-pentoxide reaction.

In the chapter on Physical Chemistry in the Golden Jubilee Number (1926) of the Journal of the American Chemical Society, Bancroft says: "At the Toronto Laboratory, under the direction of Lash Miller, work was done for several years on reaction velocity in systems containing oxidizing and reducing agents and on systems involving coupled reactions. Miller showed the inadequacy of Luther's classification of coupled reactions, without being able, however, to substitute a clear and workable classification of his own. This particular problem is one which will be solved long before the Centennial celebration."

At Baker Laboratory a start toward the study of induced reactions was made in 1927 when W. G. Vannoy submitted the reaction, chromic acid-tartaric acid induced by arsenious acid, to an investigation and found that the limiting induction factor (correction being made for extraneous influences) had not been carefully determined by previous workers, and found also that the reaction is most probably a member of Type 4 of Bancroft's classification, a complex being formed between inductor and acceptor.[26]

As a phenomenon related to the induced reaction, it may be mentioned that the passivity of iron in the presence of strong oxidizing agents has long been thought to be caused by a thin film of adsorbed higher oxide. In 1790 James Keir[27] wrote: "I put some pieces of clean fresh iron wire into a concentrated and red fuming nitrous acid. No apparent action ensued; but the iron was found to be altered . . . that is, it was rendered incapable of being attacked either by a phlogisticated solution of silver or by dephlogisticated nitrous acid. . . . The alteration thus produced on the iron is very superficial. The least rubbing exposes some of the fresh iron beneath the surface, and thus subjects it to the action of the acid." Faraday[28] in 1836 expressed more definitely the view that the passivity is caused by a film of oxide. Bennett and Burnham[29] in 1917 concluded that adsorbed higher oxide films were formed on passivated chromium, iron, and lead. "Passivity in all cases is the coating of the metal, by adsorption, with a film of a higher oxide which, being more noble than the metal, protects it from the action of the solution." They were able to show that iron dipped in a perferrate solution (iron ignited with potassium nitrate) became passive.

U. R. Evans[30] has quite lately isolated the film and calls it ferric oxide, but he has no justification for this. The film producing passivity must be a film stabilized by adsorption, as Bennett and Burnham showed, and such a film can hardly exist by itself when the actual surface upon which the adsorption occurs is removed. Evans' proof is that the film yields a blue color with ferrocyanide, but if his film were a higher oxide it would give the test for ferric iron, since ferrocyanide would reduce it to the ferric state. As a matter of fact the film will change to ferric oxide as soon as the substrate is removed. Freundlich, Patscheke, and Zocher[31] have succeeded in precipitating an exceedingly thin iron mirror on glass, and they observe that the optical properties of this film change on contact with air. It may be possible to show that this change in optical properties does not correspond to the change in optical properties when iron is oxidized to the ferric state, and thus to prove that a higher oxide is formed.

E. S. Hedges[4] has discovered a property of passive iron which is also a property of ferric oxide, indicating that the two may be identical. When passive iron is heated in solutions of nitric acid ranging in concentration from 90% to 100% (density 1.42) the first yellowing of the liquid due to the solution of the iron occurs at a temperature of 74.5° to 75.0°; and ignited ferric oxide starts to dissolve in 100% nitric acid at 75°, and in 90% acid at 72°-77°. However, there are so many properties of the passive iron film not shown by ferric oxide, that these experiments can not offer a proof of the identity of these two substances, but merely indicate the vagueness which is found throughout our meager knowledge of this phenomenon.

In the electrometric titration of dichromate with ferrous iron, the oxidizing potential unexpectedly first rises, and then drops suddenly when nearly the equivalent amount of ferrous salt has been added. This rise of potential becomes intelligible on assuming the intermediate formation of a higher oxide of iron having a potential above that of the dichromate. G. S. Forbes and E. P. Bartlett[32] in 1913 first noticed the phenomenon. The observed increment of potential was 0.2 volts. Permanganate did not produce this effect, and chlorides were found to hinder it.

N. H. Furman[33] in his study of "Bimetallic Electrode Systems for Potentiometric Titrations," found a pronounced peak in the curve for the titration of bichromate in sulphuric acid by the potentiometric method, using a Pt-Au system. Furman also obtained sharp peaks when permanganate is the oxidizing agent. It will be mentioned later how this phenomenon has been applied to the study of induced reactions by Goard and Rideal.

Baudisch and Welo[34] have called attention to the importance in biological chemistry of induced reactions in which ferrous iron is the inductor: The idea that iron salts act as catalyzers in biochemical processes, and play an important part in respiration, particularly, has gained in significance lately through the work of various investigators. The mechanism of this action of iron remained obscure, however, and one was content with the simple assumption that the variable oxidation stages were responsible for the specific catalytic power of the iron salts.

"This general assumption seems, however, to be of very doubtful validity when one considers that on a change from the ferrous to the ferric state, a very stable form is assumed which can be brought back to the ferrous state only with the use of very considerable amounts of energy. The reduction of trivalent to divalent iron is very difficult to bring about in the ordinary ionic salts of iron. Iron bound in a complex ion, on the other hand, is in general easily brought into each of the oxidation stages....

"It is known with considerable certainty that the catalytic action of the iron in respiration and many other biologically important processes is especially related to the properties of the ferrous atom or ferrous ion and not so much to the ferric atom or ferric ion."

Dhar[35] points out that when iron is administered as a drug it very probably acts though induced reactions: "Iron has long been used in the treatment of anaemia more especially of the form known as chlorosis and it was assumed tacitly that it was readily adsorbed from the alimentary tract and was utilized by the tissues to form haemoglobin. . . . If the iron is adminstered in the ferrous state, it passes into the ferric condition in the body and usually exists as a part of a complex radical and in a colloidal condition. This complex, by coming into contact with the peroxide formed from the inhaled oxygen, forms a higher oxide of iron which oxidizes food materials."

Hydrogen Peroxide as Actor

Historical

Schönbein, as has been mentioned, early observed the inductive character of the reaction[1] involving hydrogen peroxide, ferrous iron and indigo blue. He proposed the reaction as an analytical test for hydrogen peroxide, and he studied the effects of other oxidizing agents, but his work on iron was mostly of a descriptive character only.

In 1894 H. J. H. Fenton[38] used ferrous iron to induce the reaction between hydrogen peroxide and tartaric acid. Being an organic chemist he devoted his time to studying the properties of the product, dihydroxymaleic acid. He did not try to work out the quantitative relation in which the iron stood to the amount of dihydroxymaleic acid, nor did he waste many words on his simple theory. He wrote of his discovery as follows:

"When tartaric acid in aqueous solution interacts with certain oxidizing agents in presence of a trace of ferrous salt, a solution is obtained which gives a beautiful violet colour on the addition of caustic alkali. . . . Ferric salts are quite inoperative in bringing about the change; but if, in the first instance, the quantity of ferrous salt is very small, the colour produced by the alkali is greatly intensified by adding a few drops of ferric chloride." This is obviously an induced reaction since ferrous but not ferric salts produce the effect.

In 1898 he wrote:[39] "When tartaric acid is oxidized in presence of a small quantity of ferrous iron, one molecule of the acid loses two atoms of hydrogen, giving rise to dihydroxymaleic acid. The most effective oxidizing agent for the purpose is hydrogen peroxide, but the result is also brought about by chlorine, hypochlorites, bromine, etc., and by atmospheric oxygen in the presence of sunlight. The presence of ferrous iron is essential, but its proportion seems to bear but little relation to the yield of acid in the ordinary course of preparation, the action being, in fact, what is usually termed catalytic. It is necessary that the addition of the iron shall precede that of the oxidizing agent."

Then in another paragraph: "Dihydroxymaleic acid readily reduced ferric salts in the cold, experiment indicating that two atoms of iron are reduced by one molecule of the acid, so that the ferrous iron is regenerated at the expense of a portion of the acid." Thus the induced reaction is unusually complicated, and possesses the characteristics of a catalytic reaction when it once gets started. It is probably a series of three consecutive reactions involving two intermediate products: the higher oxide of iron, and the dihydroxymaleic acid. The first intermediate reacts with tartaric acid to give the second, and part of this reduces the ferric iron that has just been formed. It is then more or less of an accident that sufficient of the dihydroxymaleic acid is let undecomposed to make this a valuable method of preparing the latter.

Fenton applied the reaction to the oxidation of many organic acids and polyhydric alcohols, finding the mixture of ferrous sulphate and hydrogen effective in some cases and ineffective in others.[38]

According to his hypothesis, the ferrous iron displaces two hydrogen atoms and forms a link between the two carbon atoms attached to the central hydroxyl groups; then, under the action of the oxidizing agent, the iron becomes trivalent, and now may be assumed to break away from the organic molecule, being no longer suitable for the link; and this breaking off has released two unsatisfied carbon bonds, which allows the oxygen to enter. Since the reaction is catalytic, this explanation or that involving an intermediate higher oxide of iron would fit equally well. If a method could be found for preventing the reducing action of the dihydroxymaleic acid, so that the reaction would be truly inductive, then the ratio of oxidized iron to oxidized tartaric acid could be obtained. This ratio would be one atom to one molecule if Fenton's explanation is correct, or one atom to three molecules if the intermediate is FeO_3, and so on.

Walton and Christensen,[39] writing on "The Catalytic Influence of Ferric Ions on the Oxidation of Ethanol by Hydrogen Peroxide," persistently make the error of calling a mixture of ferric salt and hydrogen peroxide, "Fenton's reagent." Fenton himself notes that if the ferrous iron be replaced by ferric in the experiments he performed, or if ferrous iron and hydrogen be mixed in the absence of the organic liquid and be then added to the latter, the effect is markedly different. "Fenton's reagent," then, if this mixture is to have a special name, is a mixture of ferrous salt solution and hydrogen peroxide, which however is not mixed until the substance to be oxidized is added to one or the other of the constituents of the reagent.

Wilhelm Manchot[40] at the Chemical Institute of Göttingen investigated in 1901 the reaction velocity of the oxidation of ferrous iron by oxygen, with the purpose of ascertaining to which order the reaction belonged. Knowing that ferrous ammonium sulphate oxidized very slowly in air, and that the ferrous salts of many organic acids react rather rapidly, he put measured amounts of ferrous solution and potassium oxalate or citrate or tartrate solution into separate compartments of his apparatus, and ran one into the other and started the shaking motor at the same time that he pressed the stopwatch. His apparatus was filled with oxygen and connected to a burette, the level of whose confining liquid indicated at any time just how much oxygen had been absorbed.

He obtained neither a first nor a second order constant, and he concluded that he was observing a complicated reaction. He noticed, however, that in these experiments there occurred a greater absorption of oxygen than corresponded to the ferrous content. Suspecting that this might be due to an activation of the oxygen by the ferrous iron, with concomitant oxidation of part of the organic acid, he conceived the idea of oxidizing the iron in the presence of a large amount of arsenious acid, in which case the activated oxygen ought to go quantitatively to the oxidation of the latter. He found that the mixture absorbed practically double the amount of oxygen necessary to oxidize the iron to the ferric state, and from this fact deduced the existence of an instable iron dioxide, FeO_2.

Continuing his researches in oxidation, Manchot tried the effect of different oxidizing agents on ferrous iron in the presence of an acceptor, and found that when he used chromic acid, hydrogen peroxide, or permanganate, the results could be explained by assuming an unstable higher oxide of formula Fe_2O_5. Among other oxidizing agents he tried hypochlorous acid, and here he met with some difficulty, since it oxidized the acceptor rather readily in the absence of an inductor. Tartaric acid proved to be the best acceptor of several examined; but with this he found difficulties in analyzing the reaction mixture. In the end, he found that his data pointed to FeO_3 as the intermediate compound.

A different method was used each time for calculating the three formulae, FeO_2, Fe_2O_5, FeO_3. The formula Fe_2O_5 (hydrogen peroxide, chromic acid, or permanganate as actor) was obtained as follows: The formation and subsequent decomposition of the intermediate higher oxide can be expressed thus:

$$2FeO + (n+1)O = Fe_2O_{3+n} = Fe_2O_3 + nO.$$

To a large excess of acceptor and actor a small known quantity of ferrous iron was added, such that all the iron would be oxidized quickly to the ferric state. The amount of decomposed acceptor was determined, calculated in terms of equivalents, and then the number of equivalents of oxygen activated by one equivalent of ferrous iron was calculated, which is the n of the above equation.

The formula FeO_2 (oxygen as actor) was obtained more directly: The actual amount of oxygen absorbed was known, and this went ultimately to ferric iron and to acceptor. The ferrous iron was used in such small quantity that it was completely oxidized in a short time. Thus the amount of oxygen going to the acceptor for every equivalent of iron could be calculated in equivalents, the results being the n of the above equation.

The formula FeO_3 (hypochlorous acid as actor) could not be obtained so simply because of the difficulties previously mentioned. By a method of trial and error, Manchot found that when ferrous salt and hypochlorous acid in the ratio of 1 to 4 are brought together in the presence of a large excess of tartaric acid, the actor and acceptor are practically completely consumed. Here the four equivalents of actor are the $n+1$ of the previous equation.

Other oxidizing agents examined were so slow in their action as to make it impossible to determine what proportions of acceptor and inductor were simultaneously oxidized. These were persulphuric acid, chloric acid, bromic acid, iodic acid, and nitric acid.

Although considerable effort was made to isolate these three hypothetical compounds, all early attempts proved futile. There are, however, some data on compounds containing iron with a valence higher than three. In the terminology used by J. Newton Friend,[41] compounds of formula M_2FeO_3 in which the iron appears to be quadrivalent are called ferrates, and compounds of formula $MeFeO_4$ in which iron appears to be hexavalent are called perferrates.

The existence of the perferrates was established about 1841 by E. Fremy,[42] J. Denham Smith.[43] and Heinrich Rose,[44] and much of this work was repeated and confirmed later.[45, 46, 47, 48]. Ferrates were prepared in 1909 by L. Moeser and H. Borck,[49] and by G. Pellini and D. Meneghini.[50] Moeser and Borck prepared the barium and strontium salts using a temperature of 600° and a current of oxygen as the main conditions of experiment. Their analytical methods gave then the empirical formulae, which they wrote as $FeO_2.2SrO$, $FeO_2.BaO$, etc.

Pellini and Meneghini obtained the actual peroxide—not a salt of the acid—by the action of hydrogen peroxide on ferrous and ferric compounds. They employed the special conditions of an alcohol medium and a temperature of $-50°$ to $-70°$, and they obtained a reddish precipitate which, analyzed for iron and oxygen, gave a ratio averaging 1:1.9, indicating a formula of FeO_2 or Fe_2O_4. However they regard the FeO_2 as being analogous to barium peroxide, and as containing bivalent iron; and the iron in the Fe_2O_4 is considered to be trivalent.

D. K. Goralevich[51] (1926) fused ferric oxide, potassium hydroxide, and potassium nitrate together and obtained K_2FeO_4, or, with double the quantity of nitrate, K_2FeO_5.

H. E. Williams[52] (1915) gives several references to quadrivalent iron in the compound $K_2Fe(CN)^6$.

Experimental

Using chromic acid as actor and potassium iodide as acceptor, Manchot's experiments were repeated in this Laboratory, and the results obtained checked his own within moderate error. The important value is the amount of acceptor oxidized, which, the product being free iodine, is readily determined by titration with sodium thiosulphate solution. This value divided by the quantity of ferrous iron oxidized is the induction factor. In Manchot's experiments,[19] the factors were 1.83, 1.84, 1.87, 1.90, and in the repetition they were 1.62, 1.7, 1.83, 2.0.

Definite amounts of reagents—potassium bichromate, potassium iodide, and sulphuric acid—were added to 2500 cc. of cold distilled water, and the system was brought to 0° while being vigorously stirred. A given volume of ferrous solution was added during a minute and a half, then starch was added, and the liberated iodine was at once titrated with standard decinormal thiosulphate. The two sets of data were not obtained under identical conditions, variations undoubtedly occurring in the mean temperature, in the efficiency of stirring, and in the acidity (the acid was in each case only approximately two-normal). Experiments on the accuracy of the iodine estimation in these solutions indicated that the error was certainly less than four percent, and probably not greater than two.

A few reaction velocity experiments showed that within five minutes of the time the ferrous sulphate was added, the reaction was 97% completed. In half an hour equilibrium was practically reached, although a slow liberation of iodine continued indefinitely, indicating the occurrence of a catalytic reaction. This circumstance increased the difficulty of determining the exact end-point of the induced reaction, and thus increased the probable error.

From the data it appears that the limiting value of the induction factor is 2, which corresponds to an intermediate compound of formula Fe_2O_5. Now Schilow had shown that the induction factor varies with the acceptor-inductor ratio, and even Manchot, using a very few values of this ratio, found that the induction factor varied, although apparently not in a regular manner. In the present investigation the amounts of actor and acceptor have been kept constant, and the amount of the ferrous sulphate—the inductor—has been varied within wide limits; thus the acceptor-inductor ratio has been varied widely. It was found that the induction factor is a function of the variable acceptor-inductor ratio.

Hydrogen peroxide was used as the actor instead of bichromate, for it acts as an oxidizing agent whether acid is present or not. In an acid solution, as Manchot himself noticed, the induced reaction is retarded and the catalytic action of the ferric iron is increased. A few experiments with the reaction velocity in solutions of approximately the same acidity as used in the bichromate reaction showed that the induced reaction was virtually complete in two minutes, perhaps less, but that the iodine liberation continued so rapidly that in thirty minutes the volume of thiosulphate equivalent to all the iodine became twice the volume equivalent to the iodine for the induced reaction itself—in short, that a relatively rapid catalytic reaction was in progress. This iodine liberation was, indeed, considerably more rapid than that observed in the experiments with bichromate of approximately the same concentration as the hydrogen peroxide, measured in equivalents.

With regard to the inhibiting effect of acid on the induced reaction itself, Goard and Rideal[53] suggest that "this retardation of the iodine separation may be accounted for by supposing the initial formation of Fe_2O_5 to be retarded by the presence of hydrogen ions, since the ferrous ion is well known to be stabilized by acid."

In striking contrast to the behavior in the presence of acid, in a neutral solution or in a solution which is just sufficiently acid to prevent the hydrolysis of the ferrous ammonium sulphate, the reaction is remarkably rapid and clear-cut. The solution, after the iodine has been removed with thiosulphate, is a light yellow, precipitating a fine yellow oxide or hydrated oxide of iron after a few hours.[54, 55] Also, after a few hours, the solution turns a very faint blue, which is decolorized by a fraction of a drop of decinormal thiosulphate. This slight reaction is probably a direct interaction of hydrogen peroxide and iodide catalyzed by the ferric iron. In two experiments involving typical proportions of reagents, 0.29 cc. of decinormal thiosulphate were equivalent to the iodine liberated after the induced reaction in each experiment during ten or eleven hours. The total titres at the end of this time were 2.52 and 6.34 cc. thiosulphate.

Thus in neutral solution* the induced reaction yields an unambiguous end-point which permits a more careful examination of the reaction. This circumstance, and the observed variation of the induction factor with the acceptor-inductor ratio, suggested the following series of experiments.

Approximately tenth-normal solutions of hydrogen peroxide, ferrous ammonium sulphate, and sodium thiosulphate, an approximately two-tenth normal solution of potassium iodide, and starch (1 g of soluble starch to 100 cc. water) were employed. Measured amounts of iodide and peroxide solutions were run into one and a half liters of distilled water in a two-liter Pyrex beaker. About 15 cc. of the starch solution were added, the volume was made up to two liters with distilled water, and the whole was stirred vigorously for a minute or two. The system was kept at a room temperature of 22° to 24°. The ferrous sulphate solution was added from a burette, usually at a rate such that the drops fell almost too fast to be counted. Varying this rate from drops that fell slowly and could be counted with ease, to a stream showing almost no division into drops, made scarcely a measurable difference in the amount of acceptor decomposed.

The stirring device was a Witt stirrer with a bulb about 4 cm. long, driven by an electric motor having a disk friction drive for regulating the speed. The bulb of the stirrer was placed close to the bottom and near the side of the beaker, and the speed was regulated so as to be as great as possible without causing air to be drawn down into the solution by the vortex. This speed was, however, much increased during two of the blank runs.

As soon as the ferrous solution had been added the iodine was titrated with thiosulfate. Experiments showed that the induced reaction was complete almost as soon as the last drop had been stirred in. Through the help of a sheet of white paper placed behind the beaker, the iodine titre was obtained accurately to two drops of tenth-normal thiosulphate.

Blanks were run as follows:

The direct reaction between iodide and peroxide was examined by diluting to two liters 12 cc. of the former and 2 cc. of the latter, and stirring. In forty minutes the liberated iodine was equivalent to 0.25 cc. of N/10 thiosulphate, and in 219 minutes it was equivalent to 0.98 cc. It will be remembered that the induced reaction is complete in not over one minute.

The possible oxidation of the iodide by the oxygen of the air was tested by diluting to two liters 12 cc. of iodide, and stirring. No color was observed at the end of one and a half hours in either of two experiments, the reaction mixture of one being stirred in the normal manner, and that of the other being stirred so vigorously as to keep air bubbles moving throughout the whole volume of the solution.

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* "Neutral" is here taken to mean "no acid added"; actually, due to the hydrolysis of the ferrous salt, the solution shows a very slight acidity.

That ferrous iron does not catalyze the oxidation of iodide by atmospheric oxygen was shown by diluting to two liters 12 cc. iodide, 1 cc. ferrous solution, and several times the equivalent quantity of sodium fluoride, the purpose of the latter being to keep ferric iron out of the mixture through the formation of the ferri-fluoride complex compound. No color was observed at the end of 167 minutes, whether the solution was normally stirred or vigorously aerated.

In connection with the great difference between the behavior of the reaction in acid and in neutral solution it was mentioned (vide ante) that in the latter medium ferric iron does not catalyze the reaction between peroxide and iodide, or between oxygen and iodide, except to a negligible extent.

Table I

KI used, 12 cc. N/1

H_2O_2 used, 2 cc. N/1

Total volume, 2000 cc.

Expt.	Temp.	$Fe^{\cdot\cdot}$ used	Iodine	$Fe^{\cdot\cdot}$ consumed	Induction Factor	$R = \frac{KI}{Fe^{\cdot\cdot}}$
8	22.4	0.1	0.286	0.1	2.86	120
2	23	0.2	0.547	0.2	2.73	60
3	24	0.3	0.638	0.3	2.13	40
9		0.3	0.72	0.3	2.4	40
4		0.5	0.991	0.5	1.98	24
5		0.75	1.19	0.75	1.59	16
6		1.0	1.19	0.81	1.47	12
16		1.0	0.965	1.0	0.965	12
15		1.6	1.012	0.99	1.02	7.5
7	23.8	2.0	0.72	1.28	0.56	6
12	22	3.0	0.981	1.01	0.97	4
13		3.5	0.955	1.04	0.92	3.4
14		4.0	0.721	1.28	0.562	3

To simplify the statement of the concentrations, the amounts of iodide, peroxide, and ferrous iron are given as the product of the added volume and the normality; thus these quantities represent the volumes of one-normal solutions diluted to two liters, the total volume of solution in each case. It was desired to keep the concentration of peroxide and ferrous iron in the neighborhood of one-thousandth normal, corresponding to 2 cc. of N/1 solution in the two liters. Preliminary experiments showed that more potassium iodide than 12 cc. N/1 solution did not increase the induction factor when 1 cc. N/1 ferrous solution and 2 cc. N/1 hydrogen peroxide were used. These quantities of iodide and peroxide were kept constant in this series of experiments, and the volume of N/1 ferrous solution was varied from 0.1 to 4 cc.

In Table I the numbers under "Iodine" represent the volume in cc. of normal iodine solution; they are obtained by multiplying together the volume of thiosulphate required in the titration and its normality. The ferrous iron is regarded as being completely oxidized if there is present an excess of hydrogen peroxide after the induced reaction is over. Thus in the first six experiments the quantity of ferrous iron oxidized is the quantity of ferrous iron added. When the combined volume of normal ferrous solution and normal iodine solution exceeds 2, the volume of normal hydrogen peroxide employed, the ferrous iron oxidized is found by subtracting the quantity of normal iodine solution from 2, since in this case some ferrous iron remains unoxidized.

Although the fluctuations in the induction factor as the ferrous iron concentration increases leave much to be desired, the graph of the data makes unmistakable a conclusion which may be stated in this form: allowing for all the factors by which the quantity of iodine liberated depends on the concentration of ferrous iron, the latter, when added to an excess of potassium iodide and hydrogen peroxide at great dilution, conditions the decomposition of three equivalents of acceptor per mol of iron oxidized from the ferrous to the ferric state. Applying Manchot's method of determining the formula of the intermediate compound, this result points to the formula FeO_3, though the data are as adequately explained by the assumption of an intermediate of formula $FeO.2H_2O_2$.

The falling off of the factor as the ratio of acceptor to inductor decreases, or as the amount of ferrous iron increases, is most probably due to the interaction between the intermediate compound and unused ferrous salt: $FeO +$ intermediate $\rightarrow Fe_2O_3$. This reaction would obviously increase in velocity with increase in ferrous iron concentration, and to the extent that this occurs, the ferrous iron transfers to the acceptor a smaller amount of oxygen than the theoretical maximum.

This side reaction becomes less and less important as the ratio of acceptor to inductor is increased, as is confirmed by the data: a ratio of 30 to 1, for instance, corresponds to one of 2.8. Manchot obtained a factor less than 2 because he used too much iron—or too small a ratio of acceptor to inductor.[56] He himself admits that the side reaction occurs, and on this basis he explains the fact that his induction factors are not integers. In his experiments on this induced reaction he uses 10 cc. of decinormal ferrous ammonium sulphate, and 60 cc. of N/5 potassium iodide. This corresponds to an acceptor-inductor ratio of 12 to 1, and the induction factor he obtained was 1.8. In the present investigation a ratio of 12 to 1 gave an induction factor of approximately 1.3.

The reaction between intermediate and ferrous iron has been mentioned by others, and receives considerable support from the fact that iron cannot be passivated in the presence of a ferrous salt. It has been demonstrated to occur by Manchot,[21] who showed that when dilute hydrogen peroxide is added dropwise to dilute ferrous sulphate, a situation that would greatly favor this reaction, an end-point is reached when hydrogen peroxide and ferrous sulphate are consumed in the proportions to form a ferric salt. He determined the end-point of the reaction potentiometrically. Using the same solutions and the same method for obtaining an end-point, he showed that when the ferrous salt is added to the peroxide, this order hindering the reaction between intermediate and ferrous iron, the end-point occurs at a ratio of peroxide to ferrous salt greatly in excess of that required for the oxidation of ferrous salt to ferric.

Discussion

A different intermediate, called a ferrous perhydrol, was postulated in 1913 by C. S. Mummery,[54] who wrote the second of a series of papers on "Studies on Oxidation" under H. E. Armstrong.[57, 58] This improbable compound has assigned to it the structure, $Fe(SO_4H)(OOH)$. The hypothesis will not explain certain of the properties of induced reactions as determined by Manchot, Goard and Rideal, and others; furthermore his data are easily understood in the light of the higher-oxide hypothesis. Two points only will be considered here.

"When Fenton's agent acts as an oxidizing agent," writes Mummery, "as it is reconverted into ferrous salt in the process, it is clear that it merely undergoes reduction, exchanging OH for H." He is so intent upon seeing the depolarizing action in oxidation processes that he shows a tendency to neglect any inconsistency arising in the conclusion. If the intermediate compound were to return to a ferrous salt even momentarily on delivering itself of its oxidizing ability, it would be in a position to react with hydrogen peroxide and to reassume the intermediate form. Thus the ferrous iron would act in a catalytic manner, which is not at all verified by the facts—even those which Mummery himself observed. By "Fenton's agent" he apparently means the active intermediate compound formed in a mixture of ferrous sulphate and hydrogen peroxide. Mummery's error is that he is wrong in his premise, that the intermediate is reconverted to ferrous salt. When a mixture of ferrous sulphate and excess hydrogen peroxide acts as an oxidizing agent, the iron always ends up in the ferric form; thus if it be assumed that the intermediate undergoes reduction, it is reduced *to* ferric iron, and is therefore reduced *from* a stage of higher oxidation.

It is obvious that this hypothesis, involving catalysis as it does, fails to explain the existence of an induction factor—an equilibrium ratio between acceptor decomposed and ferrous iron oxidized. For, under the hypothesis, a trace of ferrous iron would accelerate the decomposition of any amount of acceptor, and the induction factor would in consequence tend to become infinite. Yet Manchot obtained the induction factor 2, and the present experiments show that the limiting factor is 3.

An adequate theory, Mummery mentions, must explain the fact that the "interaction of hydrogen peroxide and ferrous sulphate is one in which initially a ferrous compound is produced which is a powerful oxidizing agent." But why must it be a ferrous compound? Mummery's reasoning runs along two similar lines, as follows:

The active oxidizing agent is either a ferrous or a ferric salt. But the reaction goes quite slowly when ferric salt is used instead of ferrous. (He is speaking of the oxidation of formic acid.) Hence the intermediate compound is a ferrous salt.

Again, ferrous salt is known to be an oxygen carrier. Hence the oxygen of the hydrogen peroxide is transferred initially to the ferrous salt. But a ferric salt is not formed at once, since the oxidation of the acceptor proceeds too rapidly. Thus the intermediate is a ferrous salt.

These are not cogent proofs; they are hardly probabilities. The possibility of a third form of iron is not mentioned, yet we know of the existence of iron in other forms in the ferrates and perferrates. What everybody admits is that while an induced reaction is in progress, an oxidizing agent more active than hydrogen peroxide, is present. If ferrous sulphate is causing the hydrogen peroxide to become more actively oxidizing, the reaction belongs under Type 1: catalysis with destruction of the catalyst. That this is not the true explanation is shown by the existence of a stoichiometric proportion between the amount of ferrous iron added and the amount of acceptor that may be decomposed—this proportion is, of course, the reciprocal of the induction factor. On the contrary if an active oxidizing agent is formed as an intermediate, it is not ordinary ferric iron nor a complex of ferric iron with actor or acceptor, because when soluble trivalent iron compounds are added instead of ferrous iron, the reaction does not follow at all the same course. Two possibilities are left: a complex of ferrous iron with actor or acceptor; a higher stage of oxidation of the iron. Mummery chose the complex with actor, but his is not the correct formula, for it corresponds to $FeO.H_2O_2$, whereas the present experiments indicate that if the intermediate is a complex with actor its formula is $FeO.2H_2O_2$.

Goard and Rideal[53] in 1924 developed a beautiful electrochemical mechanism—hinted at much earlier by Luther and Schilow[22]—to explain the course of an induced reaction when it proceeds through an intermediate higher oxide, and to account for its becoming catalytic under certain conditions. They also offered further proof of the intermediate formation of iron pentoxide when hydrogen peroxide is the actor.

In its general form an induced reaction proceeding through an intermediate higher oxide can be represented as follows:

$$A + 2O = AO_2$$
$$AO_2 + B = AO + BO$$

Now the oxidizing ability, as measured with a potentiometer, of AO_2 will be higher than that of AO and BO, and the oxidizing ability of these will be higher than that of A and B. If the oxidizing ability of B lies below that of A, then, considering an excess of B present, B should be able to reduce AO_2 not only to AO, but down to A; thus A is again in a position to form the peroxide, and will act catalytically. If, on the contrary, the oxidizing ability of B lies above that of A, then B cannot reduce AO_2 lower than AO, since it cannot reduce a substance to a state lower than its own, and the reaction will be induced by A.

With cerous salts as inductor, Goard and Rideal show that when arsenite is the acceptor, the oxidizing abilities of the chemical substances present assume the induced order, and the reaction is an induced reaction; and when a reducing sugar is the acceptor, the oxidizing abilities assume the catalytic order, and the reaction is actually catalytic. In a study of the reaction between hydrogen peroxide and potassium iodide induced by ferrous iron, they find that the same relation holds between the character of the reaction and the order of the oxidizing potentials of inductor, acceptor, and oxidized acceptor—in neutral solution the reaction is induced, and in acid solution the order is altered and the reaction is catalytic.

The most interesting part of their work, however, is the development of a new method for the study of induced reactions: the use of an oxidation-reduction cell, a calomel electrode, and a potentiometer, for detecting the formation and disappearance of a substance of high oxidizing power in the reaction mixture.

Goard and Rideal find that the addition of a little ferrous ammonium sulphate solution to a solution one-thousandth normal with respect to hydrogen peroxide causes a slight rise in potential, which must be due to the formation of another oxidizing agent. This phenomenon is also shown by bichromate and ferrous salt, as has been mentioned. Buffered solutions must be used in order to prevent the superimposed effect of a potential due to change in the hydrogen ion concentration. As more of the ferrous solution is added, drop by drop, there comes a time when the potential falls off suddenly. The drop is followed by a horizontal section or even a short rise in the titration curve, and this in turn becomes a rather gentle downward slope. The end-point—the lowest part of the sudden drop—occurs at a point corresponding to the destruction of 1.5 mols of hydrogen peroxide per mol of ferrous sulphate. For the same concentrations of reagents, the general shape of the curve and a break in the curve quite near the ratio of 1.5 mols hydrogen peroxide per mol ferrous sulphate have been obtained by Manchot[21] and by the writer.

According to Goard and Rideal the peculiar form of the titration curve indicates "beyond question that the oxidation of ferrous iron by hydrogen peroxide proceeds by the formation of an intermediate compound," and since the end-point occurs at this particular ratio, "this intermediate compound must therefore possess the essential formula Fe_2O_5." The relation between this formula and the ratio of 1:1.5 (or 2:3) may be made clearer by a hypothetical equation: $2FeO + 3H_2O_2 = Fe_2O_5 + 3H_2O$. Goard and Rideal imply that the break indicates the complete disappearance of the hydrogen peroxide, and they conclude that it proves the existence of an intermediate compound of formula Fe_2O_5 *in the reaction mixture.* Manchot later verified the curve, criticized Goard and Rideal for calling it a "direct proof" of the existence of Fe_2O_5, and concluded that the curve is an indirect proof of its existence.

Goard and Rideal found that, in the neighborhood of the break, the addition of ferrous sulphate to the reaction mixture causes the potential first to drop and then to rise during at least three minutes. Experiments by the writer show that the potential is still slowly rising at the end of the eighth minute after a small addition of ferrous sulphate. Therefore there is occurring a reaction which is producing a strong oxidizing agent. Hydrogen peroxide is the only oxidizing agent originally present, and as its concentration cannot increase, another oxidizing agent is being formed, which must be a higher oxide of iron. Although the minimum in the curve corresponds to the ratio 1.5 mols hydrogen peroxide per mol ferrous sulphate, this slow formation of an oxidizing agent continues until much more ferrous sulphate has been added, in fact until the ratio has become 1.14.

This formation of a strong oxidizing agent can occur only at the expense of the hydrogen peroxide; therefore the occurrence of the reaction resulting in the formation of the oxidizing agent is proof that hydrogen peroxide is present. It follows, then, that hydrogen peroxide exists in the reaction mixture until considerably more ferrous sulphate has been added than corresponds to the formation of an intermediate of formula Fe_2O_5. Thus Goard and Rideal, and Manchot, are wrong in assuming that the break is simultaneous with the vanishing of the hydrogen peroxide. It is concluded, therefore, that while their curve is evidence for the existence of an intermediate higher oxide, the break in it offers no indication of the formula.

The existence of the break and hump is probably to be explained on the basis of the different relative velocities of the disappearance of hydrogen peroxide, and the formation and disappearance of the intermediate, influenced by the varying ferrous and ferric iron concentrations in the reaction mixture.

Heinrich Wieland,[59] who was interested in induced reactions from the point of view of biological oxidation processes, published in 1927 an account of a study of the reactions involving ferrous iron and such organic acceptors as oxy-acids, keto-acids, and amino-acids. "Not solely from the view-point of pure chemistry," he says, "do we regard the investigation of this subject as desirable. Since we consider that hydrogen peroxide is an intermediate product of biological oxidation, we are at the same time seeking a conception as to what extent this intermediate product can approach the catalytic action of iron, contained in all cell fluid, in oxidative action in the sense of a peroxydase."

Wieland repeated much of Fenton's work, determining, however, not the properties of the products of the oxidation, but the relative amounts of organic substance and ferrous iron oxidized. Instead of finding a small ratio between these quantities, as Manchot, Schilow, and others had found, he observed that the ratio varied up to 10, 20, and even 30, depending on the acceptor employed. Thus he and Fenton observed practically the same thing, that a small amount of iron would accelerate the oxidation of a large non-stoichiometric proportion of acceptor.

He admits the possibility of higher peroxides of iron, but as an explanation of the extraordinary ratios he found, he assumes that complex compounds of iron are the cause of the apparent acceleration. He made a quantitative study of the activating power of ferrous iron as a function of hydrogen ion concentration, finding that at a pH of 3.6 an optimum activation was reached when the acceptor was glycollic acid.

Throughout the investigations Wieland employed solutions so concentrated as greatly to favor the undesirable reactions. The action of hydrogen peroxide on most of the organic acceptors is quite appreciable at the concentrations he used, and the catalytic effect of ferric iron is also large. These reactions, objectionable because they tend to mask the effects of the induced reaction itself, cannot be arrested, but at great dilution their rates are so low in comparison to the rate of the induced reaction that their effect is entirely negligible. His experiments with potassium iodide as acceptor show clearly the confusing effect of high concentrations of reagents, including acid. Under these conditions the action of ferric iron becomes as great as that of ferrous, and during the first thirty seconds of the reaction, from 6 to 9 equivalents of acceptor are decomposed to one of iron oxidized. The blank run, with no iron added, shows in thirty seconds a decomposition of acceptor which is as large as 1/9 to 1/4 of the decomposition effected by the presence of iron. Thus his data are practically valueless for investigating the induced reaction.

In answer to this paper of Wieland's, Manchot[60] shortly afterward published a defense of his hypothesis of an intermediate iron pentoxide. He repeated several of the experiments performed in 1901, and by four different methods showed that to each equivalent of ferrous iron oxidized, three equivalents of oxygen disappear into the intermediate, or two are transferred to an acceptor. He repeated Goard and Rideal's potentiometric experiments with substantially the same results as the originators of the method had obtained; he repeated the induced reaction using potassium iodide as acceptor, confirming the former conclusion; but, unfortunately, he omitted to state how much ferrous iron, or what proportion of ferrous iron to acceptor, was used.

His third method is to show that when ferrous iron is added to hydrogen peroxide at great dilution, the peroxide is detectable in the reaction mixture until in the latter the proportion of reagents is three equivalents of peroxide to one of iron, and then after this point ferrous iron is detectable. His fourth method, a valuable contribution to the technique of studying induced reactions, is to dilute 20 cc. of approximately decinormal hydrogen peroxide to two liters, to add drop by drop four to six cc. of approximately decinormal ferrous sulphate (first generously diluting it) to the strongly stirred solution, and finally to back-titrate the hydrogen peroxide with permanganate.

These investigations may be criticized from the lack of attention paid to the extraordinarily rapid reaction between intermediate and ferrous iron, a reaction that undoubtedly occurs to a measurable extent even under the carefully controlled conditions employed in the fourth method. It is noteworthy that although the assumption of Fe_2O_5 will explain the results by Manchot adequately if the intermediate-ferrous iron reaction is negligible, the assumption of an intermediate of the essential formula FeO_3 will explain the results just as adequately, and moreover will not require any assumptions as to the unimportance of this disturbing reaction.

On increasing the concentration of the hydrogen peroxide solution from about 0.004 normal to 4 normal, Manchot finds that the number of equivalents of hydrogen peroxide disappearing per atom of ferrous iron increases from 3 to 24.5. This increase is explained satisfactorily on the hypothesis of a reaction between intermediate and hydrogen peroxide, whereby the latter reduces the former back to the ferrous state. "Obviously it is true," says Manchot, "that at a high concentration reactions occur which are not occurring noticeably at great dilution." It has been observed in the case of manganese and lead, that hydrogen peroxide shows the property of first forming peroxides out of them, and then of reducing these peroxides. He continues: "One may even say that this property belongs so surely to the characteristic properties of hydrogen peroxide, that as soon as the formation of an iron peroxide in the reaction mixture is assumed, this other reaction must be reckoned with."

In proof of the correctness of this hypothesis, Manchot shows that during the reaction in solutions of the greater concentrations, ferrous iron can be detected in the reaction mixture. As an indicator he uses alpha, alpha-dipyridyl dissolved in acetone, a reagent described by Blau.[61] As a check on this work, ferricyanide is used as indicator. The same results are obtained with this reagent; but it is less sensitive and much slower of action.

Even in the strong solutions of hydrogen peroxide, the reaction is not catalytic, but comes finally to an end with some hydrogen peroxide unconsumed and all the iron in the ferric and perferric conditions. This effect is easily explained through two reactions: the concentration of hydrogen peroxide is decreasing continuously, thus causing a diminution of the reducing action on the intermediate; and the interaction of the intermediate with ferrous iron is continuously converting the iron into the inactive ferric condition.

As has already been mentioned, Miss Benson[30] studied by reaction velocity methods the oxygen-carrying ability of ferrous iron in solutions containing bichromate and sulphuric acids. Her measurements indicate that the oxidation of ferrous iron by chromic acid follows a very different course depending on whether or not potassium iodide is present, and as this fact is cited as evidence against the formation of an intermediate higher oxide of iron, it may pertinently be examined here.

In Miss Benson's own words: "It has been established in the experimental part of this paper, that, in the absence of iodides, doubling the concentrations of either the acid or the ferrous salt quadruples the rate at which the iron is oxidized; while in their presence doubling the concentration of the acid multiplies it by eight or twelve, and doubling that of the iron, by two. It is hard to see how these facts can be accounted for by a theory which assumes that the 'primary reaction' is the same in both cases."

Miss Benson implies that if the induced reaction proceeds through the formation of an intermediate higher oxide of iron, the expression for the rate of disappearance of ferrous salt should be the same whether an acceptor is present or not. On the contrary this could not be true even in neutral solution, for the presence of an acceptor will influence the interaction of the intermediate compound with ferrous salt, and in acid solution a number of other complications arise. Thus, in the presence of acid, iodides are easily oxidized by air and the catalytic effect of ferric iron is greatly increased.

Consider the probable situation with regard to the effect of ferrous iron concentration on its own rate of change. Suppose the intermediate to be formed according to the following equation, and suppose the acceptor to react immediately with the product:

$$FeO + 2\,O = FeO_3$$

Then if the concentration of oxidizing agent does not change appreciably,

$$dx/dt = -k_1x$$

where x is the concentration of ferrous iron at time t. This theoretical result is just what Miss Benson obtained experimentally.

Now when no acceptor is present, the intermediate compound must decompose practically completely by reacting with ferrous iron. This may be expressed in an equation as follows:

$$3FeO + FeO_3 = 2Fe_2O_3,$$

and then the rate of disappearance of ferrous iron due to both reactions is given by

$$dx/dt = -k_1x - k_2x^3y,$$

where y is the concentration of intermediate at time t. Miss Benson found experimentally that when iodides are absent, $dx/dt = -k_3x^2$, but it is likely that, under certain experimental conditions and within experimental error, the expressions, $(-k_3x^2)$ and $(-k_1x - k_2x^3y)$, may be numerically indistinguishable. If the above chemical equations are not accurate, (if, for example, $FeO.2H_2O_2$ should be written in place of FeO_3) a very similar argument holds. Thus the experimental fact that the rate of oxidation of ferrous salt changes when a suitable acceptor is added, does not preclude the possibility of the primary formation of a higher oxide of iron; but is, on the contrary, just what would be expected if an intermediate higher oxide were formed.

Permanganate as Actor

The reaction involving potassium permanganate and sodium orthoarsenite was investigated under carefully controlled conditions, and was found, likewise, to yield an induction factor of three. So far as the writer is aware, this induced reaction has never before been investigated nor even mentioned. Its main point of interest here is that it is another induced reaction occurring in a non-acid medium, and therefore its course is not complicated by the undesirable retardation and catalytic effects which are brought into play by the presence of acid.

It was necessary to run the reaction in an alkaline solution; otherwise the arsenite would undergo oxidation by the air. Sodium bicarbonate was used as the alkali. Since ferrous iron is quickly oxidized by oxygen in alkaline solution, the reaction had to be run in the absence of air. For this purpose a filtering flask was used as the reaction vessel, and carbon dioxide was allowed to bubble through the solution and to pass out through the side-arm of the flask. Since potassium permanganate in alkaline solution is ordinarily reduced by ferrous iron only as far as the insoluble manganese dioxide, which obscures the end-point, an excess of solid sodium pyrophosphate was added. This reagent increases greatly the reducing ability of the ferrous iron, and the permanganate then is reduced to a soluble manganous salt.

The filtering flask was fitted with a three-hole rubber stopper through which passed the tip of a 10 cc. burette, the stem of a funnel provided with a glass stopcock near the stopper, and a delivery tube reaching nearly to the bottom of the flask. The other end of the delivery tube was connected by a length of rubber tubing to a cylinder of carbon dioxide. This is essentially the apparatus with which Job[62] titrated iron in alkaline solution with permanganate.

The arsenite solution was added each time directly to the clean flask. The air was washed out by inserting the stopper and passing a stream of carbon dioxide through the flask for a few minutes. To remove the air in the stem of the funnel, the latter was partly filled with distilled water, and the gas was made to bubble up through this by stoppering the side-arm of the flask with a finger and opening the stopcock for a few moments. The stop-cock must be closed again as soon as the gas is released through the side-arm; otherwise the distilled water at once drops into the flask and refills the stem with air. After washing the air out of the flask and out of the funnel stem, the ferrous solution may be added through the funnel or the permanganate through the burette, with the assurance that any oxidation which may occur is due solely to the permanganate. Care must be taken, of course, to wash down all the solution in the funnel without washing in any bubbles of air.

The induced reaction was run as follows: Fifty cc. of approximately decinormal arsenite solution and about three grams of pulverized pyrophosphate were put into the flask, and the latter thoroughly washed out with carbon dioxide. Then permanganate was added until the solution assumed a slight pink color, and this volume was taken as a blank correction. (The color would persist overnight with no noticeable change of tint, showing that under these conditions permanganate does not oxidize arsenite.) The correction volume being found, a given amount of ferrous solution, measured from a graduated pipette, was added slowly through the funnel. During this addition, permanganate was added drop by drop, but not in such quantity as to bring back the color of the blank run. The object of this procedure was to keep the ferrous iron concentration always as low as possible, thus reducing to a minimum the interaction of ferrous iron and intermediate. When the last of the iron had been added, the funnel was washed with three or four portions of water, and then with the permanganate the color of the solution was brought to that of the blank run as nearly as possible. From the amount of iron added and the corrected volume of permanganate, the quantity of arsenite oxidized and the induction factor were calculated. In Table II all numbers, except the induction factors, are volumes in cc.

TABLE II

Ferrous Iron		Potassium Permanganate n = 0.158				Arsenate = perman. − iron	Induction Factor
n = 0.05	n = 1	blank	titre	corr.	n = 1		
4.0	.2	.65	5.15	4.50	.71	.51	2.55
3.0	.15	.7	4.2	3.5	.55	.40	2.67
1.5	.075	.58	2.35	1.77	.28	.205	2.73
1.0	.05	.57	1.90	1.33	.21	.16	3.2
			1.8	1.23	.194	.144	2.88

The volumes in the column headed n = 1, are obtained by multiplying together the volumes of ferrous iron or the corrected volumes of permanganate and the normality of these solutions.

In the experiment with 1 cc. of iron, it was impossible to tell whether the permanganate titre was 1.8 or 1.9 cc. That is, with 1.8 cc. added, the solution seemed to be of the same color that the blank run had been, and after two more drops of permanganate had been added (making the titre 1.9) the color still seemed the same. Two more drops definitely made the reaction mixture darker in color. The mean of the two values is thus probably more correct than either, and this corresponds to an induction factor of 3.0.

These experiments therefore confirm the conclusion previously stated, that in the limiting, ideal case, ferrous iron possesses the ability to transfer three equivalents of oxygen to a suitable acceptor, and hence the intermediate compound may be of the formula FeO_3. Furthermore the result makes it very improbable that the intermediate compound is an addition product of actor and inductor, since, if this were the explanation, the intermediate for hydrogen peroxide would be $FeO.2H_2O_2$, and for permanganate, $5FeO.4KMnO_4$.

Oxygen as Actor

Historical

After discovering that Manchot's assumed pentoxide of iron[10], Fe_2O_5, is actually essentially a trioxide, FeO_3, it was natural to hope that experimental error had led him to the conclusion that a dioxide of iron is the intermediate when oxygen is actor, and that this case, too, would turn out to be intelligible on the assumption of an intermediate of formula FeO_3. Then whether hypochlorous acid, oxygen, hydrogen peroxide, or potassium permanganate were the actor, the reaction would follow the same general course: it would proceed through the intermediate formation of an unstable compound representable as FeO_3, and iron would present one uniform behavior toward these oxidizing agents instead of an improbable variety.

But this simple state of affairs does not exist. In the presence of ferrous iron, hydrogen peroxide will liberate iodine from potassium iodide, but atmospheric oxygen under ordinary pressure will not. This was shown in an experiment performed as a blank in connection with the study of hydrogen peroxide as actor: a dilute solution of potassium iodide and ferrous iron was thoroughly aerated by rotating the stirrer at a high speed, but no iodine was set free. Hence the assumption of only one intermediate iron compound will not explain the action of both hydrogen peroxide and oxygen. If FeO_3 were formed in each case, then in each case iodine ought to be liberated.

The manner in which Manchot investigated the oxygen-arsenite reaction has already been described briefly. It consisted in measuring the oxygen absorbed when a solution of potassium orthoarsenite and ferrous sulphate are shaken in an apparatus filled with the gas. The color of such a mixture is first a light green, and, according to Manchot, "the red-brown color of ferric hydroxide first appears when there is consumed almost double the volume of oxygen corresponding to the change from ferrous to ferric iron." Typical experiments were performed with the following proportions of reagents: 15 g. arsenious oxide, 36 g. potassium hydroxide, 100 cc. water, and 10 or 15 cc. approximately decinormal ferrous sulphate in 30 cc. of water. It was found that the absorption of oxygen continued after the iron had been oxidized—although at a much slower rate. When the observed volume of oxygen absorbed was corrected as carefully as possible for the effect of this side reaction, it compared with the calculated volume (twice that required in the oxidation of the iron alone) as shown in Table III.

TABLE III

Ferrous sulphate	Observed vol.	Calculated vol.
10 cc.	25.6 cc.	25.6 cc.
15	37.7	37.6

Practically the identical experiments were run in 1925 by James H. C. Smith and H. A. Spoehr[63] with similar results. The apparatus was slightly different and undoubtedly capable of greater accuracy. A new reagent was present in the mixture: sodium pyrophosphate, which is believed to have reacted at once with the ferrous iron to form the hypothetical complex compound, sodium ferro-pyrophosphate. This compound is rather loosely spoken of as a "catalyst," although the writers understand quite well that this complex is at once oxidized to an inactive ferric compound. The reaction is about ninety percent completed in four minutes of shaking, and the volume of oxygen absorbed is nearly twice that corresponding to the oxidation of the ferrous compound. The total volume of solution was always 150 cc. The temperature remained within a degree of 21. The oxygen absorption for ferrous sulphate heptahydrate was calculated to be 27.4 cc. under the conditions of experiment, and was found to be 27.5 and 27.6 in two experiments when the ferrous salt was shaken along with oxygen. Thus the experiments of Smith and Spoehr confirm the hypothesis of an intermediate dioxide of iron. The data for two of the experiments in the presence of arsenite are given in Table IV.

Gerhart Just[61] studied in 1908 the rate of oxidation of ferrous bicarbonate in aqueous solution when oxygen was bubbled through it. He suggested two mechanisms, one involving the assumption of a compound of formula $FeO_2(OH)_2$ in which the iron is quadrivalent, and the other, the intermediate formation of hydrogen peroxide. These mechanisms are speculative in character, and have for a basis only the experimental result that the rate of disappearance of ferrous iron is proportional to the concentration of ferrous iron and to that of oxygen. Thus the reaction is monomolecular with respect to iron and to molecular oxygen.

TABLE IV

Ferrous salt	$KAsO_2$	Oxygen absorbed	Calculated for twice as much ferrous salt
0.5 g.	.490 g.	26.7 cc.	27.4 cc.
0.3	.490	17.2	16.4

Experimental

In the present investigation the oxygen-arsenite reaction, induced by ferrous iron, was studied in a manner quite different from that of Manchot; yet it yields the same general conclusion, namely that in this reaction the intermediate compound may be of the empirical formula FeO_2. The induction factor persisted in remaining low until an excess of sodium pyrophosphate was added. This reagent, by forming a slightly ionized compound with the ferric iron, increased the activity of the ferrous salt, and lessened the side reaction discussed previously.

To calculate the induction factor of this reaction, it is necessary to determine, directly or indirectly, the quantities of iron and of arsenite that are oxidized. The quantity of iron oxidized is easily fixed by adding a known amount and shaking with oxygen until all of the iron is oxidized. Manchot, and Smith and Spoehr, did not determine the quantity of arsenite oxidized, but determined the volume of oxygen absorbed by the reaction mixture. The volume reacting with the arsenite may be readily calculated from their data by subtracting the amount which has combined with the iron. A more direct method of obtaining the data for the induction factor is to determine the amount of arsenate formed. A number of methods for this determination were tried out, but the presence of the basic ferric salt or the presence of the great excess of arsenite interfered seriously. A compromise was at last reached by titrating the arsenite left after the induced reaction is finished. This presented difficulties, since, to obtain the maximum induction factor, the acceptor must be present in very great excess. Thus, for a mixture of reasonable proportions, the total arsenite was equivalent to 62.5 cc. of approximately decinormal iodine, and when a portion of it had been oxidized in the induced reaction, the remaining arsenite was equivalent to 60.5 cc. The small amount of arsenate, therefore, could not be estimated with much accuracy. By adding an excess of iodine with an accurately calibrated pipette, however, and then backtitrating with thiosulphate in a 10 cc. burette, the accuracy of the analysis was improved.

It has been mentioned that the induction factor was low at first. This may be explained in part by the slowness of the reaction in its last stages. Although with permanganate as the actor, the reaction is almost as fast as a simple oxidation, and is complete in a very short time, the occurrence of a slowly fading end-point when oxygen is the actor shows that though the induced reaction is rapid at first, equilibrium is attained leisurely. That ferrous salt and arsenite form a complex in the reaction mixtures, is shown by the failure of a drop of such a solution (before oxidation) to bring a blue color to a drop of potassium ferricyanide solution. Ferrous salt, under the same conditions of iron concentration and of alkalinity with bicarbonate, gives a distinct, quick blue. It seems probable, therefore that the retarding of the induced reaction is due to the formation of a slightly dissociated arsenite-iron compound. J. N. Friend[65] offers the following as possibilities: $Fe_2As_2O_5$, $Fe(AsO_2)_2$. Near the end of the reaction, when the concentration of ferrous iron has decreased, say, 90 percent, the concentration of arsenite has decreased about 3 or 4 percent; thus by the application of the mass law the slight concentration of ferrous iron as ion would rapidly decrease as the oxidation continued, and its rate of reaction would decrease correspondingly.

As a reagent for increasing the reactivity of the ferrous iron, sodium fluoride was first tried; but sodium pyrophosphate was found to be more effective. In each run about three grams of pulverized pyrophosphate were added to 50 cc. approximately decinormal arsenite, a varying volume of 0.05 n. ferrous ammonium sulphate solution was slowly added with shaking, and the mixture in a liter Pyrex flask was placed in a shaking machine with a horizontal stroke of two inches, and shaken half an hour at the rate of about a hundred and fifty oscillations per minute. No additional water was added, the total volume being about 55 cc. The temperature was $22° \pm 2$.

A blank showed that no reaction occurs if the arsenite is shaken with air in the absence of ferrous iron:

50 cc. arsenite . = 62.6 cc. iodine (n = .0817) with no shaking
= 62.53 after shaking four hours
= 62.8 after shaking 32 hours and standing 64 hours.

Three induced reactions run in duplicate yielded induction factors approximating 1, Table IV.

While the values of the induction factor do not extrapolate definitely to one at zero concentration of ferrous iron, they indicate clearly that the limiting value is one. If no oxygen were transferred, the induction factor would be zero; if two equivalents were transferred per equivalent of iron, the induction factor would be two; it is assumed that the total reaction is the sum of two consecutive reactions, and hence that the Law of Combining Weights is operative. Thus the factor must be an integer, and it is on this basis that the limiting induction factor is said to be *one*. This means that for every equiva-

TABLE IV

Ferrous iron		Back titrations with thiosulphate				Induction factor
		all	n = 0.1038			
mn = 0.05	n = 1	arsenic	As_2O_3	As_2O_5	n = 1	
2	0.1	1.90	2.84 2.86	0.95	0.0987	0.987
4	0.2	1.90	3.80 3.85	1.92	0.1995	0.998
8	0.4	1.90	5.45 5.64	3.6	0.374	0.935

lent of ferrous iron oxidized to the ferric condition, one equivalent of oxygen is transferred to the acceptor, which is the result reached by Manchot and confirmed recently by Smith and Spoehr.

Discussion

The results of the experiments indicate that the induced reaction proceeds through the formation of an intermediate compound of iron and oxygen in the proportion of one atom of iron to two of oxygen. The formula will not be written FeO_2, however, but Fe_2O_4. A special, specific mechanism must be sought to explain the fact that oxygen does not oxidize sodium arsenite, but that oxygen plus another reducing agent does. It must be true that oxygen in the molecular state cannot react with arsenite but can react with ferrous iron. Now when a molecule of arsenite is oxidized, it acquires one atom of oxygen. Then if it be assumed that the ferrous iron can acquire two atoms or one molecule of oxygen at once, we have not only an explanation for the different reactivity of arsenite and ferrous iron toward gaseous oxygen, but there follows almost of itself an explanation for the peculiar accelerative effect of the ferrous iron, viz., that the intermediate compound formed by the consumption of one molecule of oxygen may decompose liberating one atom of oxygen, which is the right proportion to combine with arsenite. In the form of equations:

$$2FeO + O_2 = Fe_2O_4$$
$$Fe_2O_4 = O + Fe_2O_3$$

This view, that molecular oxygen combines with the inductor and atomic oxygen splits off, is supported by investigations on other reactions. The work of Job,[62] Baur,[66] and Engler[67] on oxidation in the presence of salts of cerium confirms it, and is, indeed, strong evidence for the whole higher oxide hypothesis, for in this reaction the intermediate compound has been isolated and shown to have the properties necessary to produce the induced reaction. A cerous salt will accelerate the oxidation of arsenite by air, and a ceric salt will not. The isolated perceric salt readily oxidized arsenate or cerous salt, itself returning to the ceric condition. The induced reaction may therefore be written:

$$CeO + O_2 = CeO_3$$
$$CeO_3 + K_3AsO_3 = K_3AsO_4 + CeO_2$$

in which the oxygen combines as a molecule and is transferred to the arsenite as an atom.

As further evidence for the widespread nature of this action of oxygen, von Baeyer and Villiger[68] showed that when benzaldehyde is oxidized in air, the oxygen combines as the molecule, forming benzoyl hydrogen peroxide, which then reacts with an acceptor (more benzaldehyde, indigo, etc) losing an atom of oxygen and yielding benzoic acid.

In their study of the oxidation of ferrous iron by oxygen, Smith and Spoehr[62] obtain reaction velocity data for a first order reaction: the half-period of the reaction remains constant during a three hundred percent increase in the proportion of ferrous salt added. They suggest that the reaction is a case of so-called "autoxidation," that the iron unites with molecular oxygen to form a "moloxide," and that this intermediate reacts with the acceptor if one is present. They make the further comment, "It may be of significance in this connection that stoichiometrically the moloxide, $FeO\text{-}O_2$, is equivalent to a ferrate.*"

They assume that the ferrous atoms combine singly with the oxygen, and that on this account and since the oxygen pressure was made constant, the reaction appears to be monomolecular. Following this line of thought, the simple molecule, $FeO\text{-}O_2$, would be the most likely substance to be formed. But if this were true, the volume of oxygen absorbed would not be twice the volume equivalent to the ferrous iron, but four times this volume. Since, however, the experimental data show the former value—twice the volume—the empirical formula of the intermediate may be FeO_2. The relations between the empirical formulae and the volumes of absorbed oxygen may be made clearer through hypothetical equations:

$$Fe_2O_2 + O_2 = Fe_2O_4 = Fe_2O_3 + O$$
$$Fe_2O_2 + 2O_2 = 2(FeO\text{-}O_2) = Fe_2O_3 + 3O$$

In the first equation the equivalent of iron reacts with $1/2\ O_2$, which is just double that required to oxidize the equivalent of iron up to the ferric state, namely, $1/4\ O_2$. In the second equation the equivalent of iron reacts with O_2, which is four times that required to oxidize the equivalent of iron. Thus the experiments show that the second equation does not explain the phenomenon.

This conclusion makes an examination of the first equation desirable. The reaction cannot be written: $FeO + O$, for the ferrous salt is reacting with molecular oxygen; and the reaction is obviously not monomolecular if it is written: $2FeO + O_2$. However, if the sodium ferro-pyrophosphate be considered to possess the formula proposed by Pascal,[71] $Na_8Fe_2(P_2O_7)_3$, then the

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* The term "moloxide" is explained by the context as an oxide in which oxygen enters as the whole molecule. Written "mol-oxide" it is used by Welo and Baudisch[69] as an equivalent for the older term, "holoxide," invented by Traube.[70]

"Ferrate" is the older term for a salt having hexavalent iron in the acid radical; in the present thesis, following J. N. Friend,[41] the term for such a salt is "perferrate," and "ferrate" is kept for the compounds containing quadrivalent iron.

reaction can be monomolecular with respect to the iron compound, for the latter can react with molecular oxygen, and the intermediate higher oxide can reasonably be written Fe_2O_4.

Actually the reaction cannot be monomolecular even with respect to the ferrous iron, for the higher oxide can return to the ferric stage only by interaction with more ferrous iron; thus the rate of disappearance of the ferrous iron cannot be proportional to the concentration of the ferrous iron alone; it must be proportional to a term involving also the concentration of intermediate.

It has been a stumbling block in the theory of induced reactions which postulates intermediate higher oxides that, when a ferrous salt alone is oxidized in dilute solution with oxygen or hydrogen peroxide or certain other oxidizing agents, only so much of the oxidizing agent is consumed as corresponds stoichiometrically to the oxidation of the iron from the ferrous to the ferric condition. If an intermediate higher oxide be first formed, and even if it disappear through reaction with unused ferrous iron to form ferric iron, some of the iron at the end of the reaction ought still to be in the highly oxidized state; and this amount would correspond to a quantity of oxidizing agent beyond that theoretically required. Yet an error of this sort, if it does occur, is too small to be detected by the ordinary analytical method. The data of Smith and Spoehr, mentioned above, show this. The oxygen absorption calculated from the equation, $4Fe^{++} + O_2 = 4Fe^{+++} + 2O^{=}$, was 27.4 cc. at atmospheric pressure for 1 g ferrous sulphate heptahydrate, and the observed volumes for two experiments were 27.5 and 27.6 cc.

That the reaction is experimentally monomolecular (when the pressure of oxygen is constant) and that, within the limit of analytical accuracy, no over-consumption of oxygen occurs, permits the deduction of two important facts: 1) Ferrous iron reacts two atoms at a time in this oxidation; 2) The interaction of the intermediate higher oxide and ferrous iron is remarkably rapid.

Consider the fundamental meaning of "monomolecular" as applied to a chemical reaction. When Smith and Spoehr[63] say that the reaction is monomolecular, they mean actually that the half-period of the reaction is a constant, which, as is well known, is true only if the rate of change in concentration of one of the reactants or of the only reactant is directly proportional to the concentration of this reactant. Since the simplest case of this proportionality relation is one in which single molecules decompose, the relation is often loosely taken as a definition of the monomolecular reaction. There are other cases, however, involving not merely single molecules, in which the rate of change of a substance is directly proportional to the concentration of that substance. Any explanation or reaction mechanism fitting such cases must show how it happens that the rate of change is proportional to the concentration of the one component only. Of course under ordinary circumstances the rate actually is proportional to a more complicated expression, but because of their lack of delicacy, analytical methods yield data which fit the complicated expression and the simple proportion equally well. Thus when the data for the hydrolysis of an ester point to a monomolecular reaction, they are satisfying the integrated monomolecular equation, $dC_1/dt = -kC_1$, as well as they would satisfy the integrated form of the reaction velocity equation that expresses the true situation, namely, $dC_1/dt = -k'C_1C_2$, where C_1 is the concentration of ester and C_2 is the concentration of water (mols of water per liter of solution) at time *t*. The essential thing here is that C_2 is so nearly constant that for all practical purposes, and for all ordinary methods of analysis, the product of *k'* and C_2 may be regarded as being a new constant.

A hypothetical reaction to explain the oxidation of ferrous salts may be written in two steps as follows:

$$Fe_2O_2 + O_2 = Fe_2O_4$$

$$Fe_2O_2 + Fe_2O_4 = 2Fe_2O_3$$

At time *t* let *x* be the concentration in mols per liter of the reactant containing ferrous iron, and let *y* be the corresponding concentration of intermediate. Then from the first equation the rate of disappearance of the ferrous compound is given by $dx/dt = -k_1x^n$, where *n* represents the number of ferrous molecules combining at a time, and from the second equation, $dx/dt = -k_2x^ny$. Then the total rate of change of the ferrous salt is $dx/dt = -k_1x^n - k_2x^ny$. Since the reaction has been shown to be apparently monomolecular, the rate of change of the ferrous salt must be of the form $dx/dt = -kx$. This can happen only when $n = 1$, and when the term $-k_2x^ny$ is very small compared to the term $-k_1x$. In order for *n* to be 1, the ferrous iron must enter into the reaction two atoms at a time, which may be accounted for by assuming the equilibrium $2FeO = Fe_2O_2$, or by assuming that the actual reactant is Pascal's pyrophosphate.

In order for $-k_2x^ny$ to be very small in comparison to $-k_1x$, k_2 must be very small in comparison to k_1, or *y* must be very small. Now k_1 is a measure of the rate of disappearance. Since no over-consumption of oxygen occurs in this oxidation, the intermediate obviously does not pile up in the solution; hence the rate of disappearance of the intermediate is greater, probably much greater, than its rate of appearance; thus k_2 is greater than k_1. Therefore *y* is a very small quantity, probably at least a thousand times smaller than *x*. Thus may be explained how it happens that the oxidation as a whole follows the velocity relation of the monomolecular reaction.

Conclusions

1. The induced reaction in which ferrous iron plays the part of inductor belongs to Type 3 of Bancroft's classification, the acceptor reacting with a higher stage of the inductor.

2. When ferrous iron is acted upon in neutral solution by hydrogen peroxide, or in alkaline solution by potassium permanganate, the intermediate compound formed has the essential formula FeO_3.

3. When ferrous iron is acted upon in alkaline solution by oxygen, the intermediate compound has the essential formula Fe_2O_4.

4. In an induced reaction involving ferrous iron as the inductor, the acceptor is decomposed because the intermediate higher oxide is a more powerful oxidizing agent than the actor.

5. The difference between the action of hydrogen peroxide and potassium permanganate, and oxygen, must be ascribed to the electrochemical potentials of peroxide and permanganate being greater than that of oxygen.

6. Manchot's discovery that different oxidizing agents yield different intermediate compounds is thus confirmed. That he obtained the wrong formula, Fe_3O_5 for the compound when hydrogen peroxide or potassium permanganate is actor was due to a fortuitous choice of concentrations of the reagents.

7. From potentiometric data Goard and Rideal concluded erroneously that the intermediate had the formula Fe_2O_5. The conclusion was based on the incorrect assumption that a sudden drop in their curve indicated the disappearance of the hydrogen peroxide. Actually this portion of the curve yields no hint of what the intermediate higher oxide may be.

Acknowledgment

Professor Wilder D. Bancroft has been the inspiration for this experimental research as well as the director of it. Feeling that association with him during the past four years has greatly helped the writer to appreciate the meaning and the method of chemical research, the latter gratefully thanks him for his helpful counsel and generous assistance.

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PREPARATION AND EVALUATION OF HYDROSULFITES*

6-815
7-1141

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Introduction

Hydrosulfites are used for many purposes: the estimation of oxygen in gases and the removal of oxygen from technical gases, the estimation of nitro-compounds and dyestuffs, the manufacture of dyestuff intermediates and drugs, and the bleaching of textile fabrics (especially wool and silk), leather, glue, gelatin, soap, oils, fats, et cetera.[3] The most commonly used hydrosulfite is that of sodium. It can be prepared chemically in many ways, and, electrolytically, by the reduction of a solution of sodium bisulfite.

Purpose of Investigation

The purpose of this investigation was three-fold: to ascertain the most favorable conditions for the electrolytic preparation of sodium hydrosulfite, to study the effect of the varying factors on the chemical preparation of this compound, and to find a good laboratory method for the determination of the hydrosulfite formed.

Determination of Hydrosulfite formed

Before studying the chemical and electrolytic preparation of hydrosulfite, it was necessary to find a laboratory method for the evaluation of the hydrosulfite, a method in which sulfites, thiosulfates, or any other decomposition product did not interfere, and one that did not require elaborate apparatus or rare reagents. For this purpose, a careful review of the various methods described in the literature was made. A resumé of these methods is here given. For the sake of convenience, they have been classified as those requiring elaborate or air-tight apparatus, and those not requiring it.

The following methods require air-tight apparatus:

1. Ekker[4] placed the liquid to be tested in a flask from which all the air is driven out by hydrogen, nitrogen, or carbon dioxide, any free acid is neutralized, and a small quantity of ferrous-ammonium sulphate is added as indicator. The standard solution of potassium ferricyanide (80 grams per liter; 1 cc. = 0.02114 gram of sodium hydrosulfite) is then added until the

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1465

solution becomes blue in color which disappears as soon as all the hydrosulfurous acid or hydrosulfite is oxidized, an excess of potassium ferricyanide forming with the ferrous-ammonium sulphate Turnbull's blue. Potassium ferricyanide is a good reagent for this purpose, as it is not affected by sodium bisulfite, but is at once converted by the hydrosulfite into a ferrocyanide.

G. Bruhns[1] has modified this method by adding the dry salt to a definite amount of the standard potassium ferricyanide with sufficient ferrous sulfate to form a blue, colloidal solution of Turnbull's blue, but not a precipitate. The end-point in the modified method is indicated by a change of color from blue to bright reddish-yellow. This modification depends for its accuracy on skill in dusting the powdered salt into the ferricyanide solution. Bruhns states that there is a small error due to oxygen dissolved in the solution, but that this is probably under 0.5%.

2. Another method involving direct titration with a salt, a cupric salt in this instance, is that of Bernthsen.[2] Ammoniacal cupric sulphate is the salt used, with commercial indigo as indicator. The air-tight apparatus employed consists of a three-necked Woulf's bottle, the entire tubulus of which is fitted with a double-bored cork carrying two drawn-out pieces of glass tubing which are attached by short pieces of rubber tubing to two burettes, one containing the sodium hydrosulfite solution, and the other the indigo solution. The open end of the hydrosulfite burette is closed by a U-tube filled with pieces of pumice which have been saturated with ferrous sulphate and dipped in a solution of soda. The solutions used are (a) the standard copper solution made by adding ammonium hydroxide in excess to an aqueous solution of 4.5346 grams of crystallized copper sulphate and diluting to a liter with water free from air, (b) the standard indigo solution which contains enough commercial indigo (sodium indigo sulphate) in a liter of water to make its strength equal to that of the copper solution. Fifteen to twenty-five cc. of the copper solution are placed in the apparatus, air is expelled by a current of hydrogen which enters the tubulus (having first passed through a U-tube containing ferrous hydroxide and pumice) and escapes at the third neck of the flask through a bent tube the end of which dips under water. The hydrosulfite solution is added slowly until the blue of the copper is nearly destroyed. One or two drops of indigo are next added, and the hydrosulfite carefully dropped in until the blue color is entirely destroyed. Each cubic centimeter of the Cu solution = 1 mg. of sodium hydrosulfite.

E. L. Helwig[3] used this method, but added the sodium hydrosulfite in small quantities to a measured amount of standard cupric sulphate solution in a flask through which carbon dioxide was being passed. The reaction is

$$2CuSO_4 + 4NH_3 + Na_2S_2O_4 + 2H_2O = Cu_2SO_4 + Na_2SO_3 + (NH_4)_2SO_3 + (NH_4)_2SO_4$$

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This "Copper Method" is described by N. Fradiss[1] also, who adds that, since free sulphurous acid decolorizes copper solutions, but sulphites and bisulphites do not, it is essential to neutralize the solutions to be tested.

E. Bosshard and W. Grob[2] describe a means for carrying out this determination in an atmosphere of pure nitrogen or hydrogen, so that no separation of metallic copper occurs.

The following methods do not require air-tight apparatus, and may be classed as to those that are based on the separation of a metal, a metallic oxide, iodine, or sulphur, those concerned with the formation of a formaldehyde-hydrosulfite compound, and those involving the oxidation of the hydrosulfite by a standard dye solution or by hydrogen peroxide.

3. Messrs. Brotherton & Co., Ltd. of Leeds, England, use, along with the Indigo-Carmine Method, a method proposed by A. Seyewetz and Bloch.[3] About 0.4 gram of sodium hydrosulfite is accurately weighed out in a dry stoppered weighing bottle. A silver solution is prepared by dissolving 1 gram of silver nitrate in 10 cc. of distilled water and adding 15 cc. of 20% ammonia. This solution is poured on to the solid hydrosulfite, and the reacting substances are well mixed together with a thin glass rod. After about 5 minutes, the grey precipitate of silver is filtered off on to a Gooch crucible, washed thoroughly with dilute ammonium nitrate solution until free from silver nitrate, dried ignited, and weighed in the usual way. Two hundred and sixteen parts of silver are equivalent to one hundred and seventy-four parts of pure, anhydrous sodium hydrosulfite.

J. H. Smith[4] used an ammoniacal solution of silver chloride, proceeding in the same manner as Seyewetz and Bloch, but, after washing well the precipitated silver with dilute ammonium nitrate, placed the Gooch crucible in nitric acid, warmed to dissolve the silver and to remove the nitrous acid. The crucible is removed, the solution diluted and titrated with 0.1 N KCNS solution (Volhard Method). The equation representing the reaction is:

$$Na_2S_2O_4 + 2AgCl + 4NH_4OH = 2(NH_4)_2SO_3 + 2NaCl + 2H_2O + 2Ag$$

The calculation is based on the fact that 1 mol of sodium hydrosulfite is equivalent to 2 mols of KCNS. This method is accurate and more rapid. Smith's method is an improvement on that of Seyewetz and Bloch, because, in the latter, insoluble impurities in the hydrosulfite are caught in the Gooch crucible and weighed, thus making the method inaccurate.

4. E. Orloff[5] based his method on the reduction of mercuric-potassium iodide to metallic mercury by the hydrosulfite, and the subsequent deter-

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[1] N. Fradiss: Copper method for estimating hydrosulphurous acid, Bull. de l'Assoc. de Chim. de Suc. et de Dist., **16**, (5) 453-454 (1898).

[2] E. Bosshard and W. Grob: Titration with ammoniacal Cu solution, Chem. Ztg., **37**, 437-439 (1913).

[3] A. Seyewetz and Bloch: Determination of Hydrosulfites and Hydrosulphite Compounds, J. Soc. Chem. Ind., **25**, 394 (1906).

[4] J. H. Smith: The Estimation of Sodium Hydrosulfite, J. Am. Chem. Soc., **43**, 1307-1308 (1921).

[5] E. Orloff: Analyse der Lösungen hydroschwefligsaurer Salze, Chem. Centr., **1**, 692-693 (1905).

mination of mercury by standard iodine solution. The mercuric-potassium iodide contains 60 grams mercuric chloride and 260 grams potassium iodide per liter. An excess of this solution is mixed with an equal volume of 50% potassium hydroxide and a measured amount of the hydrosulfite solution. Mercury is at once liberated according to the equation:

$$HgI_2.2KI + K_2S_2O_4 + 4KOH = Hg + 4KI + 2H_2O + 2K_2SO_3.$$

The separated mercury is filtered on to a plug of asbestos, washed well with water, and placed in a 10% solution of sodium hydroxide, and an excess of N/10 iodine solution added. The solution is then acidified with HCl, the excess iodine solution coloring the liquid a reddish-brown, mercuric iodide being first formed, thus:

$$Hg + I_2 = HgI_2$$

The excess iodine is determined by titration with N/10 sodium thiosulfate, 1 cc. of N/10 iodine being equivalent to 0.01031 g. $K_2S_2O_4$ or 0.0087 g. $Na_2S_2O_4$. In the course of our experiments, it was found that consistent results were obtained by allowing the separated Hg to remain in the NaOH solution for some time before acidification and subsequent titration. Methods 3 and 4 have been found to be very satisfactory, because they do not require complicated apparatus and because neither sulphites, nor thiosulphates, nor bisulphites interfere. Both methods have been used in the experimental work of this research, results of both methods agreeing within 1.0%.

5. A new method has been proposed by E. Knecht[1] in which advantage is taken of the fact that hydrosulfites are oxidized quantitatively to sulphites by alkaline solutions of chromates:

$$2\,Na_2CrO_4 + 3\,Na_2S_2O_4 + 2NaOH = 6Na_2SO_3 + Cr_2O_3 + H_2O$$

whereas sulphites are without action on such solutions. One-tenth to two-tenths of a gram of solid commercial hydrosulfite is added to 20 cc. of N/10 potassium dichromate which has been made alkaline with an excess of caustic soda; the solution is boiled for 4 or 5 minutes; the precipitated chromium hydroxide is separated and boiled with water and sodium peroxide until it has dissolved and the excess sodium peroxide has been destroyed. The solution is acidified with H_2SO_4, and the chromium estimated by adding an excess of standardized titanous chloride and titrating back with iron alum, or by the ordinary ferrous sulphate method.

6. A method that does not require elaborate precautions for the exclusion of air, but which is applicable only to the estimation of hydrosulfites free from soda ash and decomposition products, is that of S. H. Wilkes.[2] A weighed amount of the dry salt or a measured volume of sodium hydrosulfite solution is added to an excess of KIO_3 and KI (in the ratio of 6 g. KIO_3 to 10 g. KI). The steps involved are the reduction of the iodate, the liberation of iodine which oxidizes the sulphite formed, and the liberation

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[1] E. Knecht: New Method of Valuing Hydrosulfites, J. Soc. Dyers & Col., 31, 94 (1915).

[2] S. H. Wilkes: A New Method of Analyzing Sodium Hydrosulfite, J. Soc. Chem. Ind., 42, 356T (1923).

of more iodine from the iodate-iodide mixture by the HI formed. If there is always an excess of the iodate-iodide mixture present, the action of the sodium hydrosulfite on the iodate-iodide mixture is as follows:

$$3\ Na_2S_2O_4 + 4KIO_3 + 2KI = 3I_2 + 3Na_2SO_4 + 3K_2SO_4.$$

The iodine liberated is not directly titrated with standard thiosulphate, but the latter is added in excess to the iodate-iodide mixture before the hydrosulfite is added, and the unused thiosulphate is back-titrated with standard iodine solution. This would be an ideal method, were it not for the fact, that sodium hydrosulfite in solution is very readily reduced to sodium thiosulphate, thus giving a lower yield than one really has. This is especially true in the electrolytic preparation of sodium hydrosulfite, since sodium thiosulphate is produced simultaneously with the hydrosulfite according to the equation:

$$2NaHSO_3 + 4H = 2Na_2S_2O_3 + H_2O,$$

as well as by the decomposition of the newly-formed hydrosulfite:

$$Na_2S_2O_4 + H_2 = Na_2S_2O_3 + H_2O$$

7. Dry H_2S has no effect on dry $Na_2S_2O_4$, but, in the presence of water, rapid reaction takes place quantitatively, according to the equation:

$$Na_2S_2O_4 + H_2S = Na_2S_2O_3 + H_2O + S$$

The liberated sulphur can be readily collected and weighed.[1]

8. It has been known[2] for a long time that sodium hydrosulfite, in the presence of an excess of formaldehyde, breaks up into a mixture of sodium sulphoxylate formaldehyde and sodium bisulphite formaldehyde, according to the equation:

$$Na_2S_2O_4 + 2CH_2O + 4H_2O = NaHSO_2, CH_2O, 2H_2O + NaHSO_4, CH_2O, H_2O$$

R. W. Merriman,[3] used this fact as a basis for his method. Since sodium bisulphite formaldehyde is not acted on by iodine in neutral or acid solutions, and sodium sulphoxylate is, standard iodine solution is used to determine the amount of hydrosulfite present. The following equation shows the action of iodine on a solution of sodium hydrosulfite with an excess of formaldehyde:

$$Na_2S_2O_4 + 2CH_2O + 4H_2O + 4I =$$
$$NaHSO_4 + CH_2O + 4HI + NaHSO_3, CH_2O, H_2O.$$

The formaldehyde is mixed with water in a graduated flask and shaken until a uniform mixture is obtained. While the liquid in the flask is given a whirling motion, the carefully-weighed sample of hydrosulfite is poured into the flask through a short-stemmed funnel. The funnel is washed down rapidly with water, the volume made up to the mark, and the flask again shaken vigorously

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[1] F. S. Sinnatt: Action of H_2S on Sodium Hydrosulfite, J. Chem. Soc., **106**, ii, 460 (1914).

[2] Max Bazlen: Zur Kenntniss der hydroschwefligen Säure, Ber. **38**, 1064 (1905); L. Baumann, G., Thesmar, and J. Frossard: Formaldehyde-Hydrosulfite of Sodium, J. Soc. Chem. Ind., **23**, 1211 (1904).

[3] R. W. Merriman: The Estimation of Sodium Hydrosulfite, J. Soc. Chem. Ind., **42**, 290, Review (1923).

for some time. After a uniform mixture is obtained, a measured volume is removed by means of a pipette and placed in a beaker. An excess of standard iodine solution is added in known volume, and the resulting light-brown liquid allowed to stand for some time (about 2 or 3 minutes according to the directions of Merriman) before determining the excess iodine. In the course of our experiments with this method, we found it better to allow the hydrosulphite to remain with the formaldehyde for about fourteen hours.

A scheme proposed by R. E. Crowther and A. D. Heywood[1] consists in adding to 800 cc. of air-free water in a liter flask 40 cc. of 40% formaldehyde solution and 10 cc. of 30% NaOH solution and, while vigorously agitating the flask, adding 8-12 grams of dry hydrosulfite powder through a dry funnel. The volume is then adjusted to 1000 cc. This formaldehyde-hydrosulfite solution is then run from a burette into 25 cc. of standard methylene blue solution (14 g./L.) to which 10 cc. of glacial acetic acid and 50 cc. of water have been added, the liquid being gently boiled during the titration. The end-point is indicated by a sharp change from a bluish-green to yellow. For very accurate work, a stream of CO_2 is passed through the flask containing the methylene blue solution. Alternately, the formaldehyde-hydrosulfite solution may be added to an excess of the methylene blue solution and the excess titrated with titanous chloride.

9. Oftentimes, an excess of a standard dye solution alone is added to the hydrosulfite to oxidize it. The solid sodium hydrosulfite is added to a solution of methylene blue, and the excess of the dye is titrated with titanium chloride. This method,[2] as well as the last described, requires reagents that are uncommon, for, in the average laboratory, a dye of standard purity is difficult to obtain.

10. Since each molecule of sodium hydrosulfite, by complete oxidation with hydrogen peroxide, produces one molecule of free sulphuric acid, F. S. Sinnatt[3] has devised a method for the estimation of hydrosulfite, using this fact as a basis. About 0.6 g. of the hydrosulfite powder is slowly added to mixture of 25 cc. of N caustic soda and 50 cc. of hydrogen peroxide of about 10 volume strength. The hydrosulfite rapidly dissolves; the mixture is then heated to expel the excess of peroxide, and the excess of caustic soda is determined by titration with N sulphuric acid. According to Sinnatt, the results agree very well with those obtained by the reduction of methylene blue. Care must be taken to allow for any free sulphurous acid.

Experimental

Methods of Evaluating the Hydrosulfite

After much study and experimenting with the foregoing methods, four were chosen to use on a sample of commercial sodium hydrosulfite, in order

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[1] R. E. Crowther and A. D. Heywood: Valuation of Hydrosulfite, J. Soc. Dyers and Col., 36, 279-281 (1920).

[2] E. Knecht and E. Hibbert: Bestimmung des Hydrosulfits, Ber., 40, 3819-3827 (1907).

[3] F. S. Sinnatt: Valuation of Commercial Hydrosulfites, J. Soc. Chem. Ind., 29, 421 (1910).

to note an agreement or disagreement in their results. Table I shows the results of these experiments. The numbers in parentheses refer to the correspondingly numbered sections in the description of the methods.

TABLE I

Comparison of Methods

Method	Wt. of sample used	Wt. of $Na_2S_2O_4$ found	Average per cent purity
(1) as modified	0.2597 g.	0.2114 g.	
by G. Bruhns	0.2636 g.	0.2114 g.	80.74
(3) Silver	0.1175 g.	0.0977 g.	
	1.0637 g.	0.8695 g.	82.425
(4) Mercuric potassium iodide	0.1896 g.	0.1591 g.	
	0.2731 g.	0.2264 g.	83.385
(4) A	0.1625 g.	0.1368 g.	
	0.4136 g.	0.3449 g.	83.80
(8) Formaldehyde	1.6132 g.	1.3717 g.	
	1.7944 g.	1.5295 g.	85.25

(4) A is exactly the same as (4) except that after precipitating the Hg, it is dissolved in HNO_3, the solution evaporated to dryness, three cc. of conc. HNO_3 added, and the volume made up to 125 cc. The weight of the dissolved Hg was then determined by depositing it on a weighed Pt electrode in a Frary apparatus.

It will be noted from the above data that the method of Bruhns, involving the dusting of the solid sodium hydrosulfite into a measured amount of potassium ferricyanide containing enough ferrous sulphate to produce a colloidal solution of Turnbull's blue, gives the lowest per cent purity. This can be easily accounted for, since Bruhns admits the existence of an error of at least 0.5% due to the oxygen dissolved in the solution. Too, skill in dusting the hydrosulfite into the ferricyanide is a vital factor in the accuracy of this method. On the other hand, the formaldehyde-hydrosulfite method shows the highest per cent purity, a result which is probably due to the fact that there is less possibility of oxidation of the hydrosulfite in this procedure as compared with the other methods.

Electrolytic Preparation

The electrolytic method of preparation of hydrosulphites has not been very extensively investigated, according to the scant, indefinite information obtainable from the literature. While there is no account of any series of experiments to show definitely, clearly, and completely the relative effects of the various factors influencing the electrolytic production of this compound, there are two articles worthy of note. The first is that of Elbs and Becker,[1]

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[1] K. Elbs und K. Becker: Versuche zur elektrochemischen Darstellung unterschwefligsauren (hydroschwefligsaurer) Salze, Z. Elektrochemie, 10, 361-365 (1904).

who, from results of some of their work in this field, contradicted the statements of D.R.P. 125207 of A. R. Frank. Though the article gives a few tables, the work of Elbs and Becker is by no means exhaustive. For instance, the effects of only two concentrations, of two different cathodes, and of one temperature only, are included, in their paper. They mention using a Zn cathode in many special cases, but give no data as to the yields with this cathode. Frank,[1] in a defensive response to Elbs and Becker, describes his experiments concerning the electrolytic preparation of the hydrosulfites of sodium and calcium. However, no specific details are given, except that platinum electrodes, sodium bisulphite as cathode solution, and sulphuric acid as anode solution were used. Frank[2] asserts that sodium hydrosulfite can be obtained by the electrolysis of sodium bisulfite in concentrated, as well as dilute solutions. Again, however, he gives no data as to yields. He admits that "in his searchings he could not obtain stable sodium by electrolysis." He then turned to the electrolysis of calcium bisulphite of which salt he claims to have obtained a solution containing 55 grams SO_2 in a liter, though Elbs and Becker maintain that the highest concentrated solution possible contains only 9.3 grams per liter.

Experimental Work

The plan of the work in investigating the electrolytic preparation of sodium hydrosulfite is, in general, similar to that of the investigations of the aforesaid writers. One essential point of difference, however, is that, in the following experiments, no special precautions were taken as to the exclusion of air.

Electrolytic Vessels and Electrodes. The apparatus employed consisted of a 400 cc. Pyrex beaker as anode chamber, and a porous cup, 100 cc. in capacity, as cathode chamber. The porous cup was fitted with a cork carrying the conducting wire, a thermometer, and a sampling tube. The anode, in all the experiments, consisted of two platinum spirals. Though A. R. Frank used only a platinum gauze as cathode, Elbs and Becker mention the use of several cathodes; a nickel gauze which was not so good, a lead plate which was not useful because of the formation of a poorly conducting coating of lead sulphate, a perforated aluminum plate and a platinum gauze both of which served well (though the latter was preferred) and, finally, a zinc plate which was very satisfactory. It was found in this investigation that both mercury and amalgamated zinc cathodes gave equally high, and in several cases, higher yields of sodium hydrosulfite as did the zinc cathode. Results are recorded of experiments in which zinc, amalgamated zinc, tinned iron, pure tin, mercury, and a platinum gauze were used as cathodes. The size, as well as the nature, of the cathode was varied.

Anode and Cathode Liquids. The cathode liquid was always 100 cc. of freshly prepared sodium bisulfite. Dilute sulphuric acid (1.224 sp. gr.), 10%

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[1] Albert R. Frank: Die Darstellung des Natrium- und Calciumsalzes der hydroschwefligen (unterschwefligen) Saure durch Elektrolyse, Z. Elektrochemie, 10, 450 (1904).

[2] A. R. Frank: Process of producing Salts of Hydrosulphurous Acid, Electrochemical & Metallurgical Industry, III, 2, 72.

sodium sulphate (anhydrous). 10% sodium hydroxide, and 10% sodium chloride were the cathode liquids used.

Temperature. Experiments were performed in which the temperature of the cathode liquid was 3° ± 2° C., 10° – 15°C., and 30°C.

Current Density. The current densities used were: 0.6 amp. per sq. dcm., 2 amp. per sq. dcm., 2.34 amp. per sq. dcm., 3 amp. per sq. dcm., and 5 amp. per sq. dcm.

Experimental Results

Table II shows the effect of varying current concentration.

TABLE II

Effect of Varying Current Concentration

Cathode solution: 100 cc. 5% $NaHSO_3$
Cathode : Mercury (0.16 sq. dcm. in area)
Temperature: 15° ± 2°C.
125% theoretical amount of electricity

Current Concentration per 100 cc. solution	Hydrosulfite formed Duplicate experiments	Average per cent conversion
0.6 amp.	1.777 g.	
	1.620 g.	40.649
2.0 amp.	1.606 g.	
	1.507 g.	37.25
2.34 amp.	1.4919 g.	
	1.50 g.	35.87
3.00 amp.	1.335 g.	
	1.348 g.	32.085
5.00 amp.	0.994 g.	
	1.0971 g.	25.02

It is evident from the above results that an increase in the current concentration causes a noticeable decrease in the per cent conversion.

Table III shows that, although four of the above liquids serve well as anode liquids in the production of sodium hydrosulphite, the highest yields were obtained with sulphuric acid (sp. gr. 1.224).

In Table IV are recorded the results of experiments which indicate the relative merits of various cathode materials.

As will be noted from the above table, the various cathode materials are arranged in the order of their decreasing efficiency, amalgamated zinc and pure zinc being the most efficient.

Other experiments were tried in which the conditions were the same as those enumerated in Table IV, except that 200% of the theoretical amount of electricity was passed. The yields of hydrosulfite under these conditions are recorded in the Table V.

TABLE III

Effect of Different Anode Liquids

Cathode Solution: 100 cc. 5% $NaHSO_3$
Cathode: Zinc (1 sq. dcm. both sides)
Current Density: 2.35 amp./sq. dcm.
100% theoretical amount of electricity
Temperature: 25°C.

Anode Liquid	Hydrosulfite formed (Duplicate experiments)	Average Material Yield in per cent of theory
10% NaOH	0.65116 g.	
	0.78822 g.	17.22
10% NaCl	0.8226 g.	
	0.8913 g.	20.50
10% Na_2SO_4	1.0623 g.	
	0.8567 g.	22.96
1.224 H_2SO_4	0.9930 g.	
	1.1997 g.	23.77

TABLE IV

Effect of Different Cathode Materials

Cathode Solution: 100 cc. 5% $NaHSO_3$
Current Density: 2 amp./sq.dcm.
Area of Cathode (both sides): 1 sq. dcm.
125% theoretical amount of electricity
Temperature: 5 ± 2°C.

Cathode Material	Hydrosulfite formed (Duplicate experiments)	Average material yield in per cent of theory
Amalgamated Zinc	1.7657 g.	
	1.868 g.	43.48
Zinc	1.8726 g.	
	1.8165 g.	43.15
Platinum Gauze	1.609 g.	
	1.530 g.	37.29
Pure Tin*	1.4625 g.	
	1.404 g.	34.29
Tinned Iron*	1.0824 g.	
	1.009 g.	25.02
Zinc	1.6844 g.	
(0.16 sq. dcm. both sides)	1.695 g.	40.43
Mercury	1.636 g.	
(0.16 sq.dcm.)	1.547 g.	38.05

* In experiments with tin cathodes, the cathode liquid became dark brown in color and the cathodes were coated black, later becoming brown.

TABLE V

Conditions same as in Table IV, except that 200% of the theoretical amount of electricity was passed.

Cathode Material (0.16 sq. dcm.)	Hydrosulfite formed (Duplicate experiments)	Average Material in per cent of theory
Mercury	1.1747 g.	
	1.0570 g.	26.71
Amalgamated Zinc	0.830 g.	20.00
Zinc	0.8885 g.	21.02

The results show that decomposition takes place very rapidly after an excess of the theoretical amount of electricity has been passed. The above data seem to indicate that decomposition is more rapid with the zinc cathodes than with the mercury cathodes.

The data in Table VI show the effect of varying the current density.

TABLE VI

Effect of Varying the Current Density

Cathode Solution: 100 cc. 5% $NaHSO_3$
Current Density: 2 amp./sq.dcm.
Temperature: 3° ± 2°C.
125% theoretical amount of electricity

Cathode Material	Hydrosulfite formed (Duplicate experiments)	Average Material yield in per cent of theory
Amalgamated Zinc	1.7657 g.	
0.9 sq. dcm.	1.868 g.	43.48
(both sides)		
0.16 sq.dcm.	1.658 g.	
(both sides)	1.681 g.	40.43
Zinc		
0.9 sq.dcm.	1.7475 g.	
(both sides)	1.7821 g.	42.21
0.16 sq.dcm.	1.6844 g.	
(both sides)	1.695 g.	40.434
Mercury		
0.16 sq.dcm.	1.508 g.	
	1.475 g.	35.69
0.377 sq.dcm.	1.636 g.	
	1.547 g.	38.05

These results indicate that, as the current density increases, the yield decreases slightly.

The results obtained by varying the temperature are enumerated in Table VII.

TABLE VII

Effect of Temperature

Cathode Solution: 100 cc. 5% $NaHSO_3$
Current Density: 2 amp./sq.dcm.
125% theoretical amount of electricity

Temperature	Hydrosulfite formed (Duplicate experiments)	Average material yield in per cent of theory
Hg cathode (0.16 sq.dcm.)		
5 ± 2°C.	1.636 g.	
	1.547 g.	38.05
15°C.	1.561 g.	
	1.609 g.	37.925
30°C.	1.511 g.	
	1.433 g.	35.225
Pt gauze cathode (1 sq.dcm. in area both sides)		
5°C.	1.609 g.	
	1.530 g.	37.29
15°C.	1.263 g.	
	1.374 g.	31.55
Tinned Iron Cathode (1 sq.dcm. in area both sides)		
5° ± 2° C.	1.0824 g.	
	1.009 g.	25.02
15°C.	0.965 g.	
	0.9033 g.	22.35
30°C.	0.4132 g.	
	0.514 g.	11.09

In every instance, an increase in temperature caused a lowering of the yield of hydrosulfite. The greatest lowering appears in the case of the tinned iron.

In Table VIII are found the yields when only a certain per cent of the theoretical amount of electricity has been passed.

The highest material yield was obtained when 125% of the theoretical amount of electricity was used. This yield was 38.64%. There was a gradual lowering in the yield, as electricity in excess of the theoretical amount was passed.

TABLE VIII

Cathode Solution: 100 cc. 5% $NaHSO_3$
Cathode: Hg (0.16 sq.dcm. in area)
Current Density: 2.34 amp./sq.dcm.
Temperature: 3°C.

Am't of Electricity in per cent of theory	Hydrosulfite formed (Duplicate experiments)	Average Material yield in per cent of theory
50	1.1817 g. 1.1817 g.	28.25
100	1.2700 g. 1.2806 g.	30.50
125	1.4732 g. 1.5832 g.	38.64
150	1.3570 g. 1.3930 g.	32.90
175	1.2681 g.	30.34
200	1.2105 g.	28.96

In an effort to increase the yield, solid $NaHSO_3$ was added in the course of the electrolysis. Table IX shows the results.

TABLE IX

Cathode Solution: 100 cc. 5% $NaHSO_3$
Cathode: Zinc (1 sq.dcm., both sides)
Current Density: 2 amp./sq.dcm.
Temperature: 7°C.

Electricity in per cent of theory	Hydrosulfite formed (Duplicate experiments)	Average Material yield in per cent of theory
200 (no salt added at 100% electricity)	1.506 g. 1.561 g.	36.72
200 (2.5 g. solid $NaHSO_3$ added at 100% elect.)	1.9312 g. 1.8426 g.	33.23

The data in the above table show that, although the yield was not increased by the addition of solid $NaHSO_3$ during the course of the electrolysis, one was able to produce a stronger solution of the hydrosulfite.

Tables X, XI, XII, and XIII show the effect of increasing the concentration of the $NaHSO_3$.

TABLE X

Cathode Solution: 100 cc. 10% $NaHSO_3$
Cathode: Zinc (1 sq.dcm., both sides)
Current Density: 2 amp./sq.dcm.
Temperature: 18°C.

Ampere hours passed	$Na_2S_2O_4$ formed	Theoretical yield (current)	Average current yield in per cent of theory	Increase in grams of $Na_2S_2O_4$
1	1.748 g.			
	1.851 g.	3.22 g.	53.35	1.7995
2	1.908 g			
	2.007 g.	6.44 g.	30.40	0.1581
3	1.987 g.			
	1.823 g.	9.66 g.	19.72	−0.0526

TABLE XI

Conditions the same as in Table X except that the cathode solution was 100cc. of 15% $NaHSO_3$.

Ampere hours passed	$Na_2S_2O_4$ formed	Theoretical yield (current)	Average current yield in per cent of theory	Increase in grams of $Na_2S_2O_4$
1	2.871 g.			
	2.670 g.	3.22 g.	84.04	2.810
2	3.348 g.			
	3.173 g.	8.44 g.	50.97	0.513
3	3.364 g.			
	3.271 g.	9.66 g.	34.34	0.0297
4	2.533 g.			
	2.383 g.	12.88 g.	19.61	−0.895

TABLE XII

Conditions the same as in Table X except that the cathode solution was 100 cc. of 25% $NaHSO_3$

Ampere hours passed	$Na_2S_2O_4$ formed	Theoretical yield	Average current yield in per cent of theory	Increase in grams of $Na_2S_2O_4$
1	3.027 g.			
	2.844 g.	3.22 g.	91.16	2.975
2	4.7559 g.			
	4.3895 g.	6.44 g.	71.005	1.653
3	5.569 g.			
	5.410 g.	9.66 g.	56.83	0.812
5	5.178 g.			
	5.017 g.	16.10 g.	31.58	−0.3405

TABLE XIII

Conditions the same as in Table X except that the cathode solution was 100 cc. of 35% $NaHSO_3$.

Ampere hours passed	$Na_2S_2O_4$ formed	Theoretical yield	Average current yield in per cent of theory	Increase in grams of $Na_2S_2O_4$
1	2.872 g.	3.22 g.	90.37	2.903
	2.928 g.			
2	5.063 g.			
	4.909 g.	6.44 g.	77.42	2.145
3	5.362 g.	9.66 g.		
	5.512 g.		56.28	0.4553
5	4.797 g.			
	4.599 g	16.10 g.	29.18	−0.7423
7	4.432 g.			
	4.508 g.	22.54 g.	19.83	−0.223

From these four tables it is easily seen that the highest initial current yield is obtained from the most concentrated solution of $NaHSO_3$. However, this initial current yield sinks rapidly, and the decomposition of the formed $Na_2S_2O_4$ soon outweighs the new formation. It can also be noted from these tables that the decrease of the yield occurs more quickly with time in the more concentrated solutions.

Chemical Preparation

Methods. (1) Sodium hydrosulfite was prepared by passing a current of sulphur dioxide into a mixture of sodium bisulphite and zinc dust (Coleman & Bell Co.). In this method, the influence of temperature, concentration of sodium bisulphite, and rate of flow of sulphur dioxide was observed.

(2) Hydrosulphurous acid was made by passing a current of sulphur dioxide into a mixture of water and zinc dust. The effect of variation of temperature was studied.

Apparatus. The sulphur dioxide was first passed through sulphuric acid and then through a U-tube filled with glass wool before it entered the Soxhlet flask containing the liquid to be acted upon.

Solutions. The solutions were: (1) 100 cc. of freshly prepared sodium bisulphite, (2) 100cc. of distilled water. The zinc dust was added to the solution.

In Table XIV, results of experiments showing the effect of temperature on the yield of hydrosulfite are recorded.

Each figure given in Table XIV is an average of the results of two different experiments under the same conditions. From the results given in this table, it can be noted that at the low temperature the highest yields are obtained. The data show also that the bisulphite method gives the highest yields of hydrosulfite.

TABLE XIV

Effect of Temperature

Rate of flow of SO_2; 7 liters per hour
Time: 1 hour

Solution	Grams of Hydrosulfite Formed at 2°C.	at 35°-40°C.	at 67°C.
100 cc. 50% $NaHSO_3$, 50 g. Zn dust	5.361	1.993	1.5163
100 cc. of distilled H_2O, 50 g. Zn dust	2.605	1.5316	1.3343

TABLE XVI

Effect of Concentration of Sodium Bisulfite

Solution: 100 cc. $NaHSO_3$ solution, 25 grams zinc dust
Rate of flow of SO_2; 7 liters per hour
Time: 1 hour

Concentration of $NaHSO_3$	Temperature	$Na_2S_2O_4$ formed (Duplicate exp.)	Average
5%	35°C.	2.3311 g.	
		2.3624 g.	2.2963 g.
10%	35°C.	2.3995 g.	
		2.4441 g.	2.422 g.
10%	36°C.	3.3276 g.	
		3.598 g.	3.4628 g.
30%	37°C.	4.6873 g.	
		5.2103 g.	4.9488 g.
50%	35°C.	5.073 g.	
		5.088 g.	5.0805 g.

TABLE XVII

Solution: 100 cc. 5% $NaHSO_3$ solution, 25 grams zinc dust
Time: 1 hour
Temperature: 48°C.

Rate in liters per hour	$Na_2S_2O_4$ formed (Duplicate experiments)	Average
3.5	2.0223 g.	
	2.0537 g.	2.03797 g.
7.2	2.2276 g.	
	2.3289 g.	2.2872 g.
10.0	2.0223 g.	2.0223 g.
20.0	1.988 g.	
	2.2964 g.	2.1422 g.

Under the same conditions as above, experiments were continued over a period of six hours; the highest concentration of sodium hydrosulfite in the liquid was 5.6795 grams at 2°C. in the bisulphite method. However, crystallization had occurred during this time.

The results of this table show that the yield of hydrosulfite increases with an increase in the concentration of the sodium bisulfite. The greatest increase occurs between concentrations of 20% and 30%.

One can easily see from Table XVII that changing the rate of flow of SO_2 from 3.5 liters per hour to 20 liters per hour has no appreciable effect on the yield of hydrosulfite.

Summary and Conclusions

1. The silver method and the potassium mercuric-iodide method have been found to be satisfactory laboratory methods for the determination of hydrosulfites. They require no elaborate apparatus for the exclusion of air, and sulphites, thiosulphates, and bisulfites do not interfere.

2. Sulphuric acid (sp. gr. 1.224) has been shown to be better than 10% anhydrous sodium sulphate, 10% sodium hydroxide, or 10% sodium chloride as anode solution in the electrolytic preparation of sodium hydrosulfite.

3. Cathodes of amalgamated zinc and mercury were found to give the highest yields of hydrosulfite.

4. Increasing the current concentration causes a noticeable decrease in the yield of hydrosulfite.

5. An increase in the current density is accompanied by a slight decrease in the yield.

6. The raising of the temperature lowers the yield.

7. The highest material yield of hydrosulfite is obtained when 125% of the theoretical amount of electricity has been passed.

8. Solid sodium bisulphite added during the process of electrolysis does not increase the yield, but it enables one to produce a more concentrated solution of $Na_2S_2O_4$.

9. The highest per cent current yield is obtained during the first ampere hour, but this good initial yield sinks rapidly, the decomposition of the sodium hydrosulfite soon outweighing the new formation. This decrease in the yield occurs more quickly with time in the more concentrated solutions.

10. A greater yield of hydrosulfite is obtained chemically by passing sulphur dioxide through a mixture of sodium bisulphite and zinc dust than by passing sulphur dioxide through a mixture of distilled water and zinc dust.

11. As in the electrolytic method, the highest yield of hydrosulfite is obtained at low temperatures.

12. Increasing the concentration of the bisulphite increases the yield of hydrosulfite.

13. Changing the rate of flow of the sulphur dioxide from 3.5 liters to 20 liters per hour does not appreciably affect the yield of hydrosulfite.

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THE SORPTION OF WATER VAPOUR BY ACTIVATED CHARCOALS

Part IV. Isothermals in Absence of Foreign Gases (Static Method)

BY A. J. ALLMAND, P. G. T. HAND, J. E. MANNING AND D. O. SHIELS

1. Introductory

In Part II of this series,[1] it was mentioned that, in the majority of previous determinations of sorption isothermals of vapours on solid sorbents, a vacuum technique had been employed. In the case of water vapour and charcoal, work of this nature has been published by Schmidt and Hinteler,[2] Bachmann,[3] Gustaver,[4] Hällström,[5] H. H. Lowry[6] and Coolidge.[7] The work of Schmidt and Hinteler and of Hällström in this connection need not detain us, as their technique would seem to have been defective, and their experiments are of little scope. The other experimenters, at whatever temperature they worked, covered the complete pressure range up to saturation. Bachmann employed an apparatus previously designed in conjunction with Zsigmondy and Stevenson[8] for investigation of sorption by SiO_2 gel. He worked with a coconut charcoal at 15°C., and obtained an isothermal showing marked hysteresis and irreversibility. Gustaver used an animal charcoal (Merck) of very high capacity, worked at about 16°C., and observed hysteresis in the intermediate relative pressure range. In his earlier work, Lowry employed charcoals which were certainly very similar to our specimens A, B and C. Working at 25°C., his isotherms were characterised by abrupt breaks in the intermediate pressure region. In his later work, carried out at 20°C. on a series of charcoals prepared from anthracite, no such breaks were obtained. Coolidge has carried out elaborate and important experiments, working over a wide temperature range and using coconut charcoals and an ash-free sugar charcoal. He concludes that irreversibility is the result of the presence of some inorganic ash constitutent. We shall take up this point at a later stage. The isothermals he obtained indicate a definite saturation value, *i.e.*, they are concave to the pressure axis in this region; those of all the other workers approach the saturation pressure asymptotically, *i.e.*, are concave to the pressure axis near saturation (see Fig. 1, Part II).

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[1] J. Phys. Chem., 33, 1151 (1929).

[2] Z. physik. Chem., 91, 103 (1916).

[3] Z. anorg. Chem., 100, 1 (1917).

[4] Gustaver: Arkiv för Kemi 8 och Geol., 7, No. 22 (1919); Kolloidchem. Beihefte, 15, 185 (1922).

[5] Dissertation, Helsingfors (1920).

[6] J. A. Chem. Soc., 42, 1393 (1920) (with Hulett); 46, 824 (1924).

[7] J. Am. Chem. Soc., 46, 596 (1924); 49, 708 (1927).

[8] Z. anorg. Chem., 75, 189 (1912).

2. Experimental

The charcoals used were A, B and C, as previously, with the addition of Charcoal D, a steam-activated mixed nut charcoal (British origin) and of Charcoal J, a sugar charcoal (British origin). Charcoal D[1], dried at 150°C., contained 3.21 per cent of ash, consisting mainly of silica, together with the carbonates and sulphates of Al, Fe, Ca, Mg, Na and K, no particular base being present in preponderating amount. Charcoal J originally contained 0.34 per cent of ash (nature not investigated). In an attempt to reduce this, it was covered with a solution of HF, slowly evaporated to dryness, heated until all fumes had been given off, and then successively extracted with boiling concentrated HCl and distilled water. The whole procedure was repeated three times and the charcoal finally washed with water until free from chlorides. The ash content was, however, only reduced to 0.29 per cent by this treatment. Charcoals D and J were used after preliminary evacuation at 270°C. and 110°C. respectively, the other three charcoals after outgassing both at 270° and 800°C. In addition, A and B, outgassed at 270°, were used after they had received a thorough extraction with HCl (Part I, p. 453).

Our experimental method has been described in Part I (pp. 448 ff.) and nothing need be added, except that it should be mentioned that, in the majority of cases, in order to avoid possibility of error due to surface condensation of water vapour, the maximum pressure worked to was rather less than 23.76 m.m., the saturated aqueous vapour pressure at 25°. The maximum pressures employed are indicated in Table II. An example of the complete data of a single run is contained in Table I, but, as before, the results as a whole will be expressed by means of isothermal diagrams.

TABLE I

Charcoal B. Outgassed at 800°C

Absorption		Desorption	
Aqueous vapor pressure in m.m.	M.g. of water per gram of charcoal	Aqueous vapour pressure in m.m.	M.g. of water per gram of charcoal
3.64	10.6	18.68	731.4
9.24	23.8	17.35	659.4
12.79	44.9	16.75	571.6
15.41	84.0	15.97	438.8
18.15	222.2	15.29	286.1
18.40	345.9	14.40	141.2
19.42	593.0	13.33	72.7
23.70	780.2	4.72	13.9
		0.00	3.36

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[1] See also Chaplin: Proc. Roy. Soc., A. 121, 344 (1928), and Allmand and Burrage: J. Soc. Chem. Ind., 47, 372T (1928). The experiments described in the present series of papers form part of a larger investigation of which it is hoped to publish the results from time to time, and, in order to make comparisons easy, the designation of any particular charcoal will remain the same, whatever the paper in which it is referred to. Thus, by Charcoal D will always be meant the same steam-activated mixed nut charcoal of British origin.

3. Results

In what follows are given:

(i) particulars regarding the outgassing process;

(ii) the increase in weight of the charcoal, compared with its original evacuated weight, after the final evacuation at 25°;

(iii) data concerning the result of subsequent evacuation of the charcoal;

(iv) the diagrams of the complete sorption-desorption isothermal.

(a) *Charcoal A—Evacuated at 270°C.*

(i) This was the first experiment, done before the standard procedure had been worked out. After 8¾ hours outgassing, including 5 hours at 250°–270°, eight sorption points were obtained. The charcoal was then evacuated at room temperature and, after readmission of air, re-evacuated for 4 hours, including 3½ hours at 250°–280°. Seven more sorption points were then obtained, the maximum pressure being 22.68 m.m. Again the charcoal was exhausted and re-evacuated at 250°–290° for 4 hours. It was then charged directly at 22.19 m.m pressure, and a series of seven desorption points obtained.

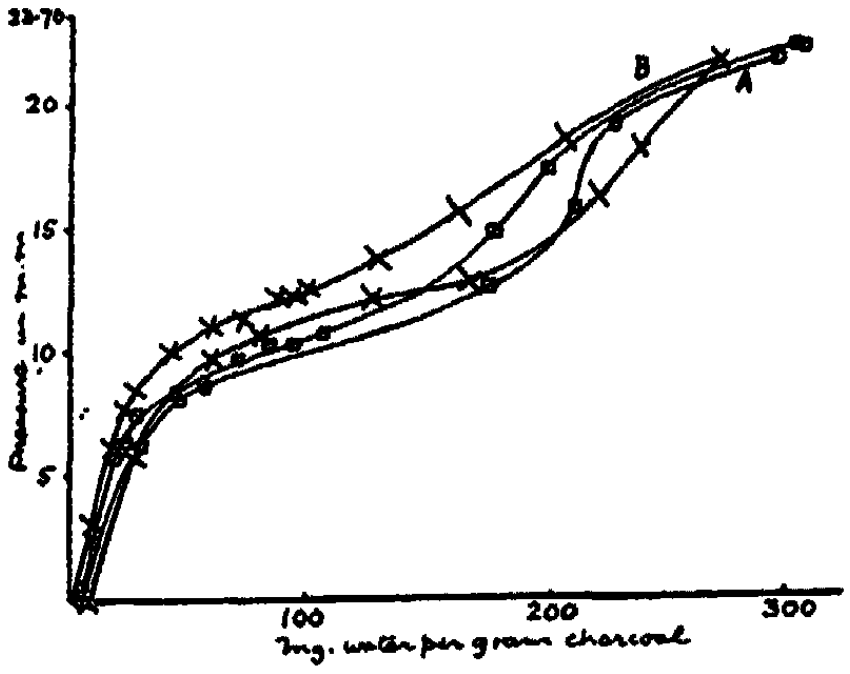

Fig. 1

(ii) 4.28 m.g./gram.

(iii) Evacuation at 250° resulted in the recovery of 3.98 m.g./gram of water. In addition, a quantity of gas was evolved, amounting to

CO_2 0.79 m.g./gram.
O_2 0.02
CO 0.23
$N_2 + H_2$ (?) 0.04 c.c./gram.

(iv) See Figure 1A.

(b) *Charcoal A—Evaporated at 800°C.*

(i) Outgassed for 9½ hours, including 6 hours at 770°–830°.

(ii) 7.67 m.g./gram.

(iii) 5.25 m.g./gram of water recovered by evacuation at 270°. The evolved gases, of which the greater part came off at the final evacuation temperature of 800°, amounted to

CO	1.3	m.g./gram
CO_2	0.35	
H_2	0.05	
O_2	0.04	

(iv) See Fig. 1B.

(c) *Charcoal B—Evacuated at 270°C.*

(i) Owing to the large amount of sublimate (Part I, p. 453) produced on heating this charcoal, and the slowness with which it is removed at 270°, the charcoal employed was subjected to a preliminary evacuation at 300° for two hours in a large silica tube, before filling into the charcoal container.

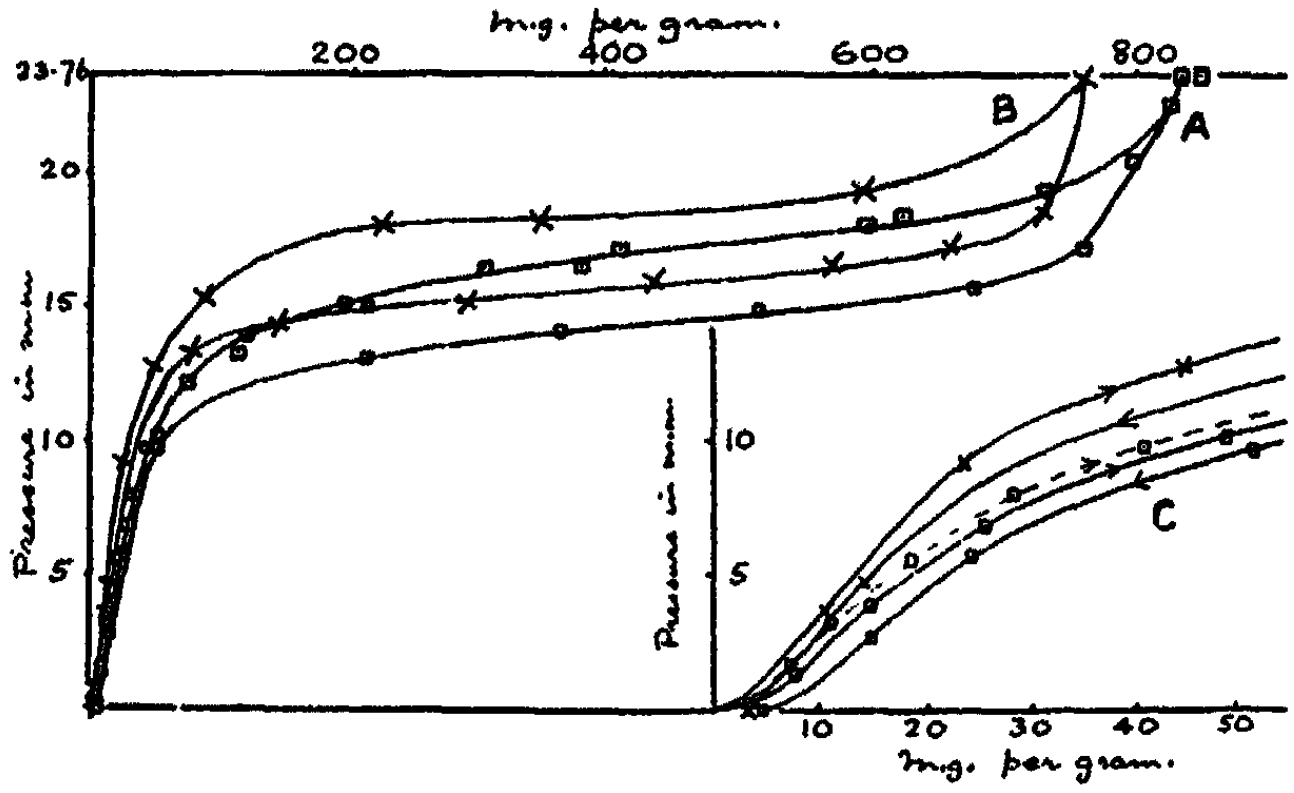

FIG. 2

Two samples of this charcoal were worked on, one being used for an adsorption experiment only, the other being employed for the complete sorption-desorption cycle. Both specimens, after filling into the container, were outgassed for 3 hours at 270°.

(ii) 4.50 m.g./gram.

(iii) 2.91 m.g./gram of water recovered at 270°. No gas was evolved.

(iv) See Figure 2A. On the sorption-branch of the curve are plotted all the points obtained in the two duplicate sorption experiments. They give a good idea of the degree of reproducibility attainable. In Figure 2C, the results at low pressures are plotted on an expanded quantity scale, the points in the duplicate sorption experiment being put on a dotted curve.

(d) *Charcoal B—Evacuated at 800°C.*

(i) After preliminary desublimation at 800°, the charcoal was outgassed at the same temperature for 7½ hours.

(ii) 3.36 m.g./gram.

(iii) Not investigated.

(iv) See Figs. 2B and 2C.

(e) *Charcoal C—Evacuated at 270°C.*

(i) Outgassed for 4¾ hours at 270°–280°. After the first desorption was completed, a partial resorption was carried out up to a pressure of 4.26 m.m., followed by a second evacuation at 25°.

(ii) 6.22 m.g./gram after complete cycle; 5.74 m.g./gram after the resorption.

(iii) 5.09 m.g./gram of water recovered at 270°. Quite negligible quantity of gas.

(iv) See Figure 3A. In Fig. 3C, the low pressure points are plotted on a doubled abscissa scale, the resorption points, which fall on the desorption curve, being denoted by triangles.

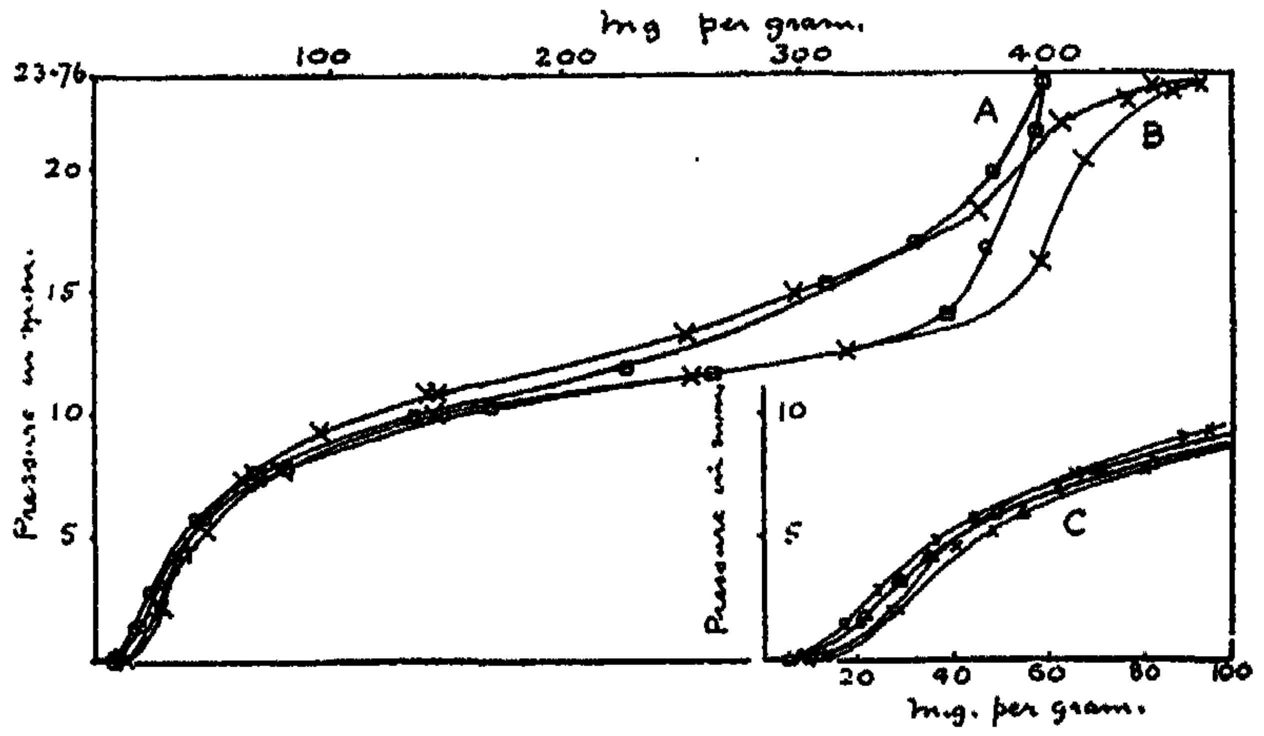

Fig. 3

(f) *Charcoal C—Evacuated at 800°C.*

(i) After preliminary evacuation at room temperature, the charcoal was outgassed at 765°–800° for 3½ hours. Two specimens were used. With one, a sorption experiment only was carried out. With the second, two successive complete sorption-desorption cycles were worked through, together with another partial resorption, followed by desorption and final outgassing. The details of the resorption curves will be considered later (see Part V, Fig. 8).

(ii) 10.01 m.g./gram after complete cycle; 10.15 m.g./gram after first resorption cycle; 9.92 m.g./gram after the second (partial) resorption cycle.

(iii) 8.86 m.g./gram of water recovered at 270°. The gases evolved at 800° (the final outgassing temperature) amounted to

CO	13.3 m.g./gram	N_2	0.08 m.g./gram
CO_2	1.2	H_2	0.07
O_2	0.14		

(iv) See Fig. 3B, in which are plotted all the points of the *first* complete sorption-desorption cycle, together with the sorption points obtained with the duplicate specimen of charcoal. The degree of reproducibility is again seen to be good. Fig. 3C contains the low pressure points plotted on an expanded quantity scale.

(g) *Charcoal D—Evacuated at 270°C.*

(i) Outgassed for three hours at 270°C.

(ii) 3.24 m.g./gram.

(iii) Not investigated.

(iv) See Figure 4A.

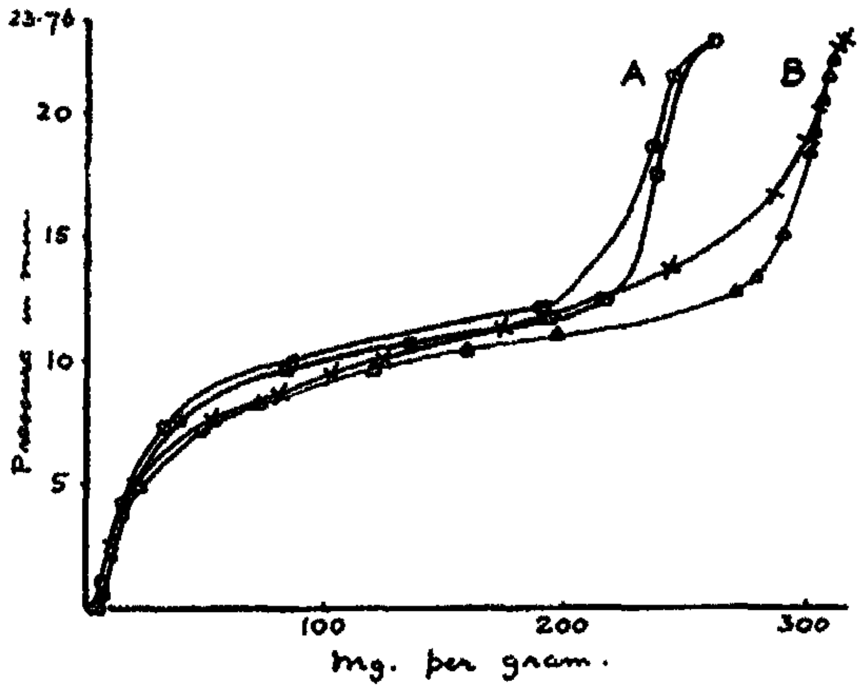

Fig. 4

(h) *Charcoal J—Evacuated at 110°C.*

(i) No details available.

(ii) 5.35 m.g./gram.

(iii) Evacuation at 110° resulted in the recovery of 1.86 m.g./ gram of water.

(iv) See Fig. 4B. In order to distinguish sorption and desorption points at pressures near saturation, where the curves coincide, the latter are plotted as triangles.

(j) *Charcoal A—Acid Extracted—Evacuated at 270°C.*

(i) Outgassed for 10½ hours, including 8½ hours at 250°–285°. After the sorption-desorption cycle had been completed, two resorption points, at 3.77 and 4.25 m.m. pressure, were determined.

(ii) 4.36 m.g./gram.

(iii) Not investigated.

(iv) See Fig. 5 (compare with Fig. 1A).

(k) *Charcoal B—Acid extracted—Evacuated at 270°C.*

(i) Outgassed for 3 hours at 270°C.

(ii) 2.32 m.g./gram.

(iii) The whole of the water, *viz.*, 2.32 m.g./gram, was recovered after two hours outgassing at 270°. No gas was evolved.

(iv) See Fig. 6 (compare with Fig. 2A).

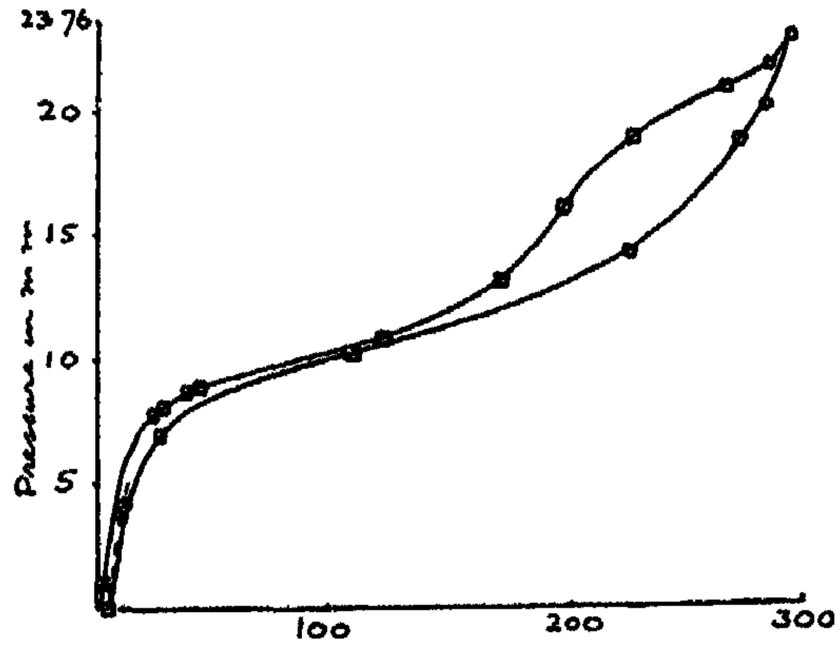

FIG. 5

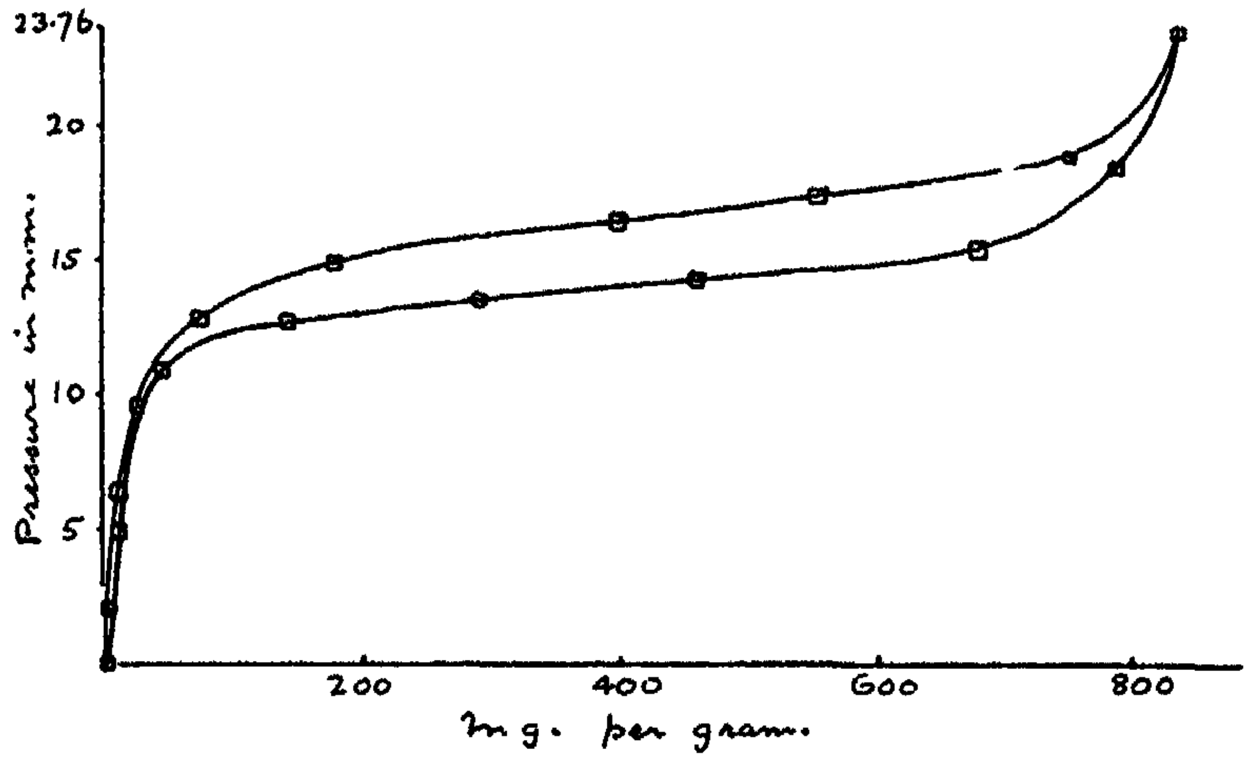

FIG. 6

4. Discussion of Isotherms obtained by the Vacuum Technique

In Table II certain of the data pertaining to the above experiments are collected together. In column 5, those values marked (E) have been obtained by extrapolation and are subject to a corresponding and variable degree of uncertainty.

All isothermals of charcoals A, B and C again exhibit hysteresis, but to a lesser extent than when working in a stream of gas, as comparison of the diagrams in this paper with those in Parts II and III will make clear. Similar differences to those already noted exist between the sorption isothermals for the different charcoals outgassed under identical conditions. Of the "270°C." charcoals, C is the best at all pressures up to about 16-17 m.m., and is then passed by B. Of the "800°C." charcoals, C again sorbs most strongly up to 18 m.m., when B passes it. The amount of water vapour taken up in this case by B is indeed about doubled by a rise in pressure from 17 m.m. to 18 m.m.; below 17 m.m. it is less efficient even than A. One feature of the experiments in the N_2-stream is again encountered, *viz.*, the change in the shape of the isothermal for Charcoal C at pressures near saturation when the outgassing temperature is altered from 270° to 800°C. —a curve concave to the pressure axis is replaced by one convex to this axis.

TABLE II

Experiment	Charcoal	Outgassing temperature	Maximum pressure used in experiment (m.m.)	Saturation figure (m.g./gram)	Water retained at zero pressure (m.g./gram)
a	A	270°	22.68	350(E.)	4.28
b	A	800°	22.10	320(E.)	7.67
c	B	270°	23.74; 23.76	851(E.); 835.2	4.50
d	B	800°	23.70	780(E.)	3.36
e	C	270°	23.47	404(E.)	6.22
f	C	800°	23.37; 23.44	500(E.)	10.01
g	D	270°	23.16	285(E.)	3.24
h	J	110°	23.25	330(E.)	5.35
j	A (acid extracted)	270°	23.37	295(E.)	4.36
k	B (acid extracted)	270°	23.76	834.4	2.32

On the whole, the effects of an increase of outgassing temperature are less definite than in the previous series of experiments. Charcoal C, as before, when outgassed at 800°, has a higher saturation figure, shows more pronounced hysteresis, and retains larger amounts of water at "zero" vapour pressure at 25°, than does the corresponding "270°C." charcoal. Charcoal B (800°) on the other hand has a smaller saturation value and retains less water after final evacuation than does Charcoal B (270°), although exhibiting more hysteresis as measured by the differences in q between isobaric points on sorption and desorption curves. Charcoal A behaves as previously found in respect both of hysteresis and of water retention after final evacuation, but, on the other hand, the relative positions of the two curves near saturation suggests that the actual saturation value would have been greater for the "270°C." than for the "800°C." charcoal.

Experiment (g) was done to enable a comparison to be made between two different steam-activated nut charcoals C and D. They are seen (Figures 3a and 4a) to show no particular similarity.

Although Charcoal J is necessarily free from any morphological structure such as persists in charcoals obtained by charring naturally occurring vegetable matter, it is of interest to note that its isothermal is of the same general type as that of other charcoals. Allowing for the fact that it is a far more efficient charcoal, its isothermal closely resembles that obtained by Rakovsky[1] for Kahlbaum sugar charcoal (16.4°C.—in presence of air). Its hysteresis loop is, however, far smaller.

Comparison between the results of experiments (a) and (c) and those of (j) and (k) should give some idea of the effect of the reduction of ash content by acid extraction. The saturation capacity of Charcoal B does not seem much affected, but that of A is appreciably lowered, due to an alteration in the shape of the sorption curve at high pressures. This is the only occasion in which we have found this charcoal to give a curve concave to the pressure axis near saturation. With Charcoal A, the quantity of water retained at "zero" pressure is slightly increased as the result of acid treatment; in the case of Charcoal B, it is practically halved. In both cases, whilst the greater part of the isotherm is but little affected by the extraction, the absorption at low pressures is decreased.

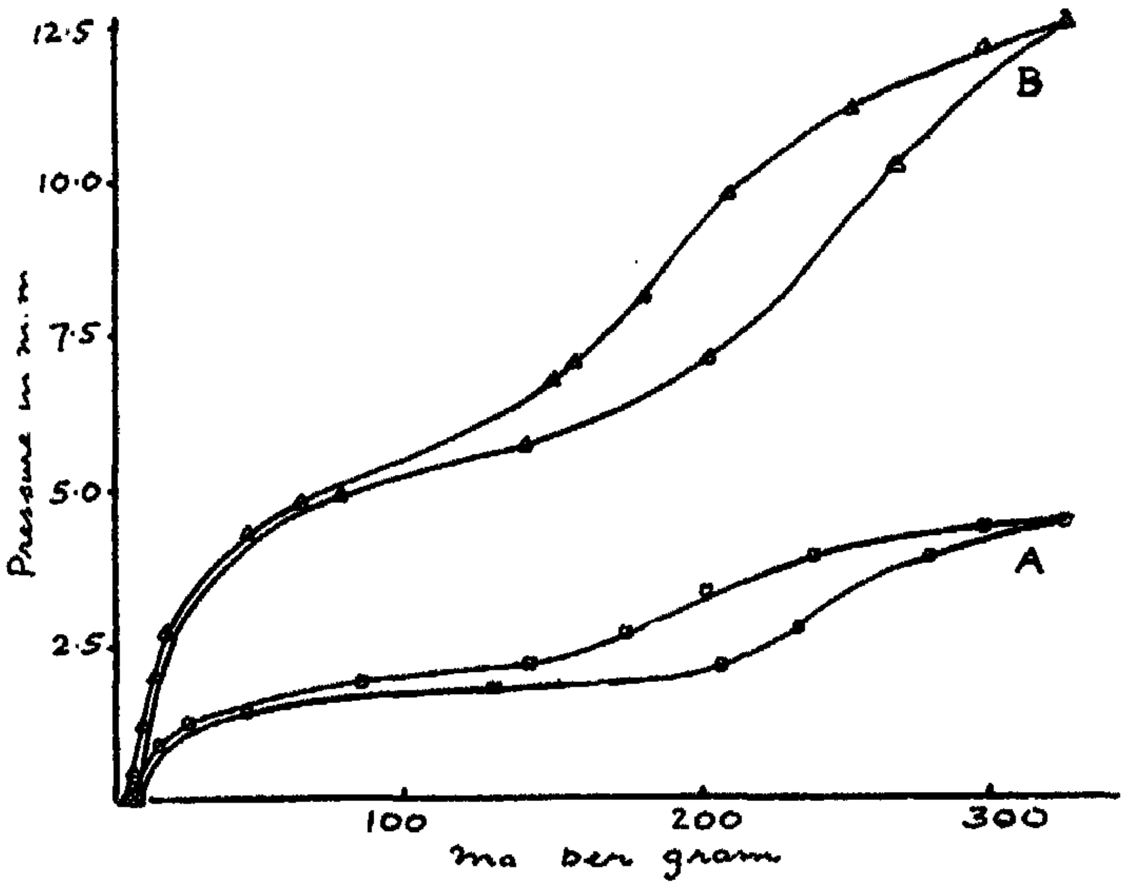

FIG. 7

5. Experiments at 0° and 15°C. Heat of Sorption of Water Vapour on Charcoal

All the experiments hitherto described were carried out at 25°. In order to obtain a general idea of the effect of temperature, measurements were also carried out on Charcoal A at 0° and 15°C. In the first case, the preliminary evacuation lasted for 4¾ hours, including 3½ hours at 250°-280°. The

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[1] J. Russ. Phys. Chem. Soc., 49, 371 (1917).

charcoal was maintained at 0° in a Dewar flask by means of stirred ice-water. After the first desorption point, a little air was accidentally admitted. The charcoal was re-evacuated for 3 hours, including $1\frac{3}{4}$ hours at 230°-280°, the "saturation" point at 4.55 m.m. determined, and the desorption curve completed. 6.36 m.g./gram of water were retained after the final evacuation at 0°. The isothermal is shown in Fig. 7A. For the isothermal at 15°, three separate samples of the charcoal, all outgassed at temperatures between 230°-290°, were used. The first seven sorption points were obtained with the first specimen, the next three points with the second specimen, and with the third specimen the remainder of the sorption and the complete desorption curves. 5.78 m.g./gram of water were retained after the final evacuation at 15°. During the determination of the isothermal, the temperature was kept at 15° by adding by hand, when required, small amounts of cold water to water contained in a Dewar flask. The isothermal is plotted in Fig. 7B.

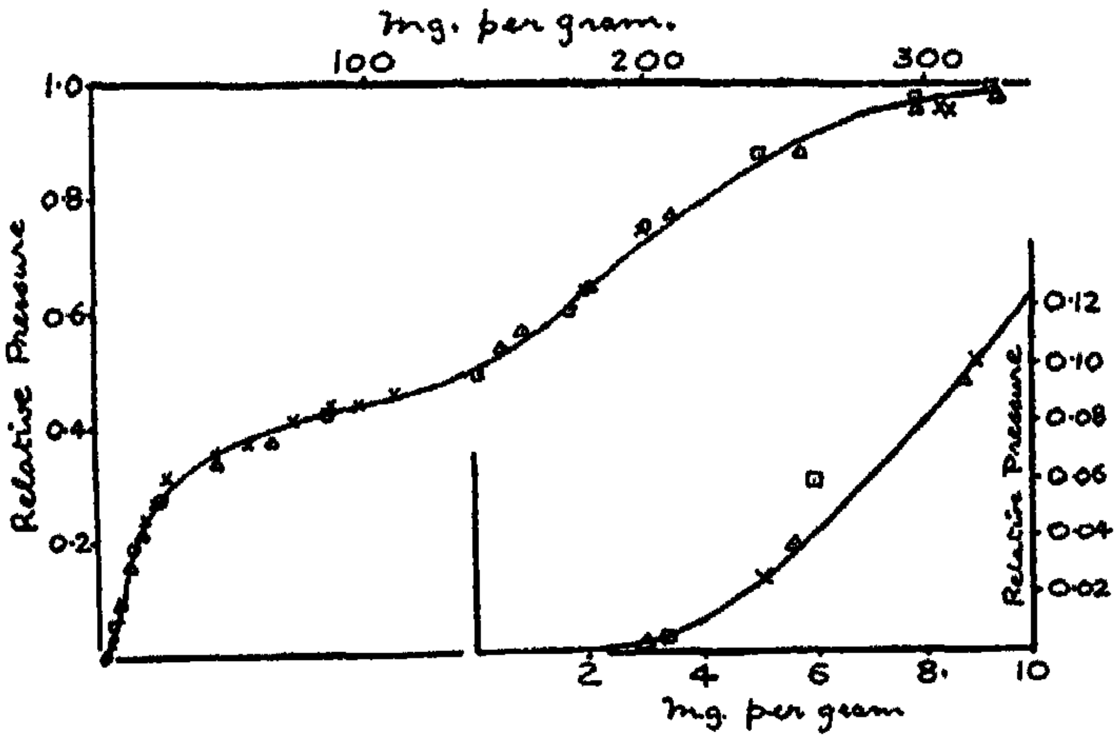

FIG. 8

□ 0° C. △ 15° × 25°

The obvious similarities between the sorption branches of Figs. 7A, 7B and 1A suggested plotting all three sets of results in the form of q against the corresponding relative pressure p/p_0. This was done, with the result shown in Fig. 8, where the seven lowest points are separately plotted on a larger scale. It is clear that, within experimental error (and it will have been evident that no great precision is claimed for any of the three isothermals concerned) all the points fall on a common curve. This means that

$$\left(\frac{\partial p/p_0}{\partial T}\right)_q = 0$$

i.e. $$\frac{1}{p}\cdot\left(\frac{\partial p}{\partial T}\right)_q = 1/p_0\cdot\frac{dp_0}{dT}$$

i.e. $$\left(\frac{\partial \ln p}{\partial T}\right)_q = \frac{d\ln p_0}{dT}$$

which, in its turn, indicates that the total heat of sorption of water vapour on this charcoal is independent of the amount of water vapour sorbed and is equal to the total heat of condensation of water vapour to liquid water.

The degree to which this is borne out quantitatively by our measurements is shown in Table III, which contains the equilibrium pressures for various values of q at 0°, 15° and 25°C., read off to the nearest 0.05 m.m. from the sorption curves of Figs. 1A, 7A and 7B, together with the values of the mean total heat of sorption per gram of water between each pair of these temperatures, calculated by the Clausius-Clapeyron equation.

TABLE III

q in m.g./gram	p in m.m. 0°	15°	25°	λ in calories/gram 0°-15°	0°-25°	15°-25°
10	0.55	1.45	2.6	561	558	553
20	1.1	2.9	6.2	561	621	718
40	1.5	4.1	8.3	555	614	668
60	1.7	4.7	9.15	562	604	631
80	1.85	5.1	9.9	560	602	628
100	2.0	5.5	10.6	559	599	621
125	2.1	6.0	11.55	607	612	620
150	2.25	6.75	12.8	635	624	606
175	2.7	7.8	14.75	614	610	603
200	3.2	9.25	17.8	614	616	620
250	4.05	11.0	20.9	578	589	607
300	4.4	12.0	11.45	580	585	593

Similar calculations have been made from the desorption curves at 0° and 15° (Fig. 7) and Table IV contains the results.

The total latent heat of condensation of water vapour has the following average values (calculated from the Clapeyron-Clausius equation)

0° – 15°	594 calories/gram
0° – 25°	591
15° – 25°	586

Our data are not sufficiently accurate to justify any detailed discussion of the divergencies from these figures exhibited in the above tables. Attention will be drawn to two points only. Whilst the heat of sorption at 10 m.g./gram has a value near (or lower than) the heat of condensation, it appears to become greater for higher values of q, finally falling off and tending towards the heat of condensation as saturation is approached. Further, the value of λ 0°-15° is throughout greater for the desorption than for the sorption process, the average difference being nearly 60 cals/gram, or about ten per cent.

TABLE IV

q in m.g./gram	p in m.m.		λ in calories/gram
	0°	15°	0°-15°
10	0.33	0.95	583
20	0.9	2.65	624
40	1.35	3.9	614
60	1.5	4.55	642
80	1.65	4.9	629
100	1.7	5.2	647
125	1.75	5.5	662
150	1.8	5.85	682
175	1.9	6.35	698
200	2.05	7.05	714
250	3.25	9.1	595
300	4.2	11.55	585

The results in this paper will be discussed later. Experiment (h) (isothermal for sugar charcoal) was carried out by Mr. A. Puttick, to whom we wish to make due acknowledgment.

University of London,
King's College,
May 28, 1929.

THE SORPTION OF WATER VAPOUR BY ACTIVATED CHARCOALS

Part V. (A) Charcoals extracted by Alkali. (B) Resorption—Lag or Drift—Hysteresis

BY A. J. ALLMAND, P. G. T. HAND AND J. E. MANNING

A. THE SORPTION OF WATER VAPOUR BY ALKALI-EXTRACTED CHARCOALS

1. Introductory

In Part IV of this series (p. 1682) are recorded experiments carried out on two charcoals which had been extracted by hydrochloric acid. The results in some respects were not conclusive, but agreed in that whilst the course of the isotherm at intermediate pressures was but little affected by the extraction, this had the effect of decreasing the amount of water vapour taken up at low pressures. The effect of temperature on the isotherm of Charcoal A having indicated (Part IV) that the nature of the sorbed water film is very similar to that of ordinary liquid water, it seemed possible that the complete removal of those inorganic ash constituents which might be supposed to have the power of retaining water vapour at low pressures might lead to the complete elimination of the low pressure portions of the isothermals, and to the production of charcoals which would not sorb water vapour appreciably until quite considerable relative pressures were reached.[1] As acid extraction, both by HCl and by H F, had proved ineffective in reducing the ash content of various charcoals below appreciable limits, extraction with alkali was tried.

2. Experimental

Charcoals A, B and C were employed, their isothermals at 25°, after extraction and outgassing, being determined by the static method. The general method of extraction has been described in Part I (p. 454). In practice, considerably longer periods of treatment, with one or all of alkali, acid and water were used in some instances. In every case, before weighing out for the determination of the sorption isothermal, the extracted charcoal was desublimated by several hours heating in vacuo at 800°C.

The following particular points may be noted.—

(a) *Charcoal B.* Ash of alkali-extracted charcoal 0.14 per cent, whereas the ash of H Cl-extracted charcoal was 0.12, and of the unextracted material 3.90, per cent.

(b) *Charcoal C.* Ash after alkali extraction 0.125 per cent, whereas the ash of HCl-extracted charcoal was 1.34, and of the unextracted charcoal 2.2, per cent. A special experiment showed that a subsequent extraction with HF reduced the ash a little further only—to 0.10 per cent.

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[1] Subsequent to our experiments, a paper appeared by Coolidge (J. Am. Chem. Soc., 49, 708 (1927)) in which this point of view was developed and thoroughly examined experimentally. We shall refer later to this paper.

(c) *Charcoal A.* Ash after one extraction 0.35 per cent (after HCl extraction 0.31, of the unextracted material 4.59, per cent.)

(d) *Charcoal A.* The charcoal from (*c*) was submitted to a second similar treatment, after which the ash had suffered reduction to 0.295 per cent. Analysis, confirmed by a microscopic examination, showed the residue to consist of aluminium silicate.

As it was thought possible that the incomplete extraction of silica and alumina by the alkali in cases (*c*) and (*d*) might have been due to slow and incomplete penetration of the most minute pores of the charcoal by the viscous alkali, a series of extractions at higher pressures was carried out, and a few sorption points determined on the resulting charcoals.

(e) *Charcoal A.* After a preliminary digestion with boiling concentrated NaOH in a nickel crucible at ordinary pressures, the charcoal was boiled with concentrated alkali in an autoclave at three atmospheres, this being done several times with fresh charges of NaOH. There followed (i) extraction with hot water until no reaction took place with phenolphthalein; (ii) 15 hours boiling with concentrated HCl; (iii) final washing with distilled water; (iv)desublimation at 800°. The ash was not determined.

(f) *Charcoal A.* (i) Preliminary alkali extraction at ordinary pressures; (ii) extraction with concentrated NaOH in an autoclave at 4-8 atmospheres pressure and 100°-130°; (iii) water extraction; (iv) extraction with boiling concentrated HCl; (v) water extraction in the autoclave at 100°-110° and 10 atmospheres; (vi) boiling with HCl; (vii) final washing at ordinary pressures with distilled water; (viii) desublimation at 800°. The ash was not determined.

(g) *Charcoal A.* First digested with concentrated HCl and washed free from chlorides; heated at 110° with concentrated NaOH at 10 atmospheres; extracted with water until there was no colouration with phenolphthalein after standing overnight; desublimated at 800°. Ash not determined.

3. Results of Sorption Experiments

In what follows are given, when on record:—

(i) particulars regarding the outgassing process;

(ii) the increase in weight of the charcoal, compared with its original evacuated weight, after the final evacuation at 25°;

(iii) data concerning the result of subsequent evacuation of the charcoal;

(iv) the diagram of the sorption-desorption isotherm.

(a) Charcoal B—Extracted by Alkali at Atmospheric Pressure—Evacuated at 800°C.

(i)Time not recorded.

(ii) 2.05 m.g./gram.

(iii) Not determined.

(iv) See Fig. 1, which also contains, plotted on a larger scale, the detail of the isotherm at low *q* values, together with the corresponding detail (triangles) for the isotherm for unextracted charcoal (see Part IV, Fig. 2B).

(b) *Charcoal C—Extracted by Alkali at Atmospheric Pressure—Evacuated at 800°C.*

(i) Preliminary outgassing at room temperature, followed by 3½ hours at 780°–800°.

(ii) 1.51; 1.58 m.g./gram.

(iii) 0.91 m.g./gram of water recovered at 270°. The gases evolved at this temperature and at 800° (the final outgassing temperature) amounted to

CO 0.66 m.g./gram
CO_2 0.21
O_2 0.07

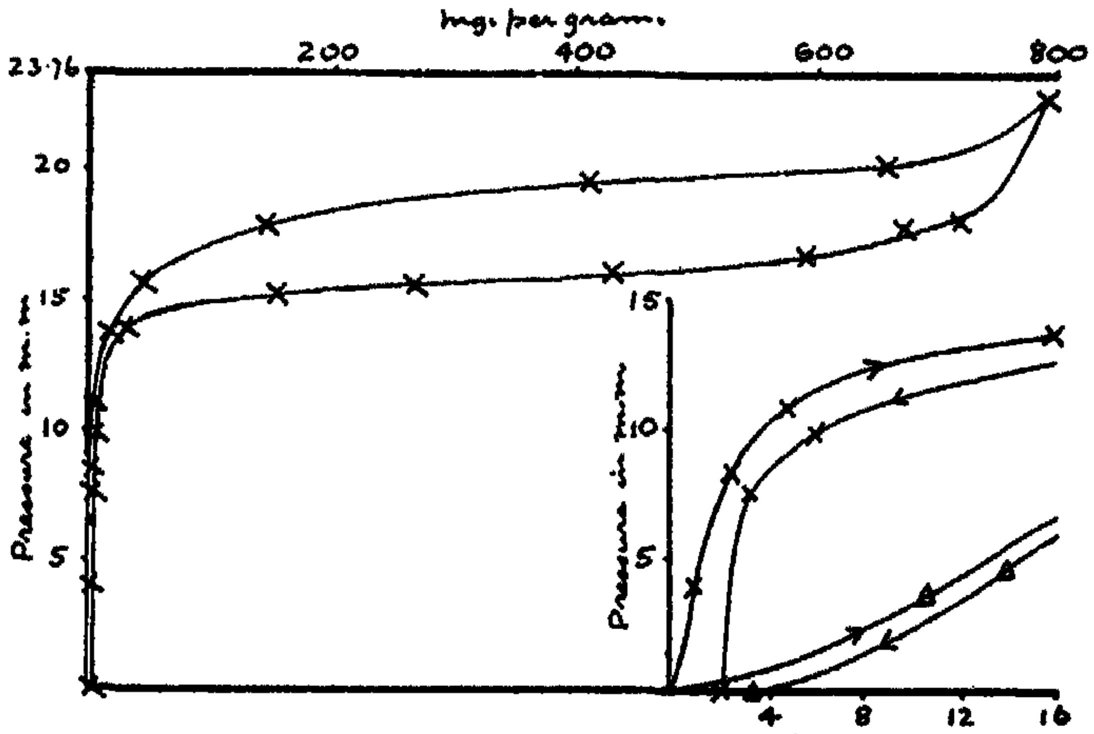

FIG. 1

(iv) See Fig. 2. After carrying out a complete sorption-desorption cycle (increase in weight at "zero" aqueous vapour pressure 1.51 m.g./gram), water vapour was resorbed up to a pressure of 16.02 m.m., and then again desorbed down to 13.38 m.m., the whole constituting Series II. Lastly, two more resorption points were measured, the maximum pressure reached being 16.78 m.m., a desorption point at 16.53 m.m. then determined, and the charcoal finally once again evacuated at 25°, the increase in weight over the original evacuated weight of the charcoal being 1.58 m.g./gram. These results will be considered later on in this paper. Fig. 2 also contains, plotted on a larger scale, the detail of the isotherm at low *q* values, together with similar detail for the unextracted charcoal (see Part IV, Fig. 3B).

(c) *Charcoal A—Extracted by Alkali at one Atmosphere Pressure—Evacuated at 800°C.*

(i) Outgassed for three hours at 800°.

(ii) 3.15 m.g./gram.

(iii) Not determined.

(iv) See Fig. 3A.

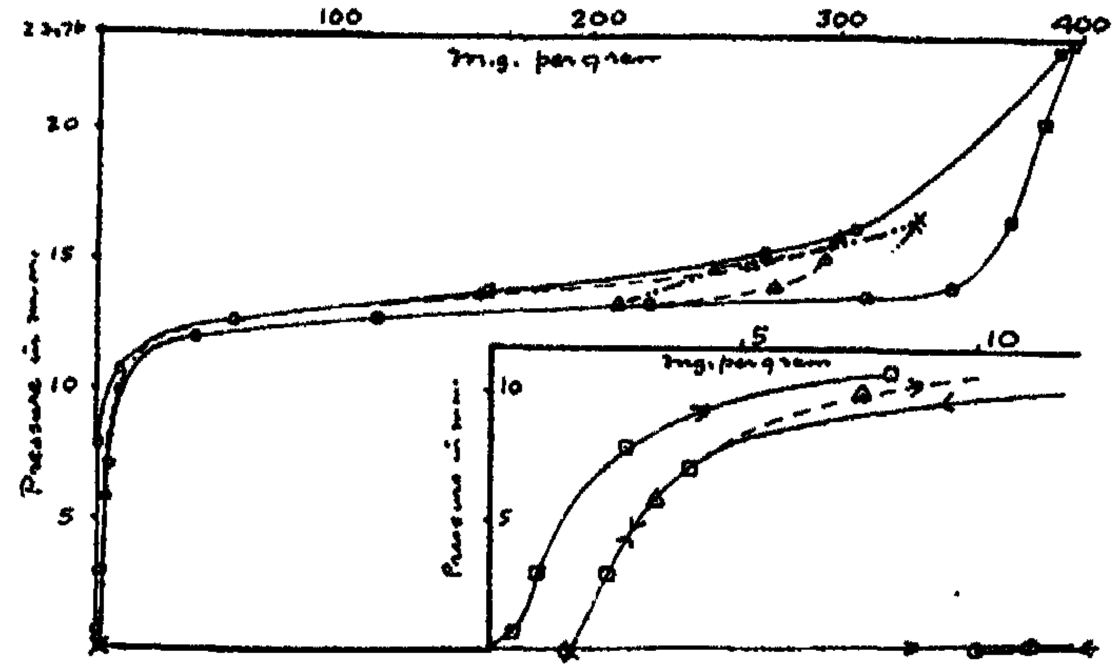

FIG. 2

Series I □
II △
III ×
Unextracted ○

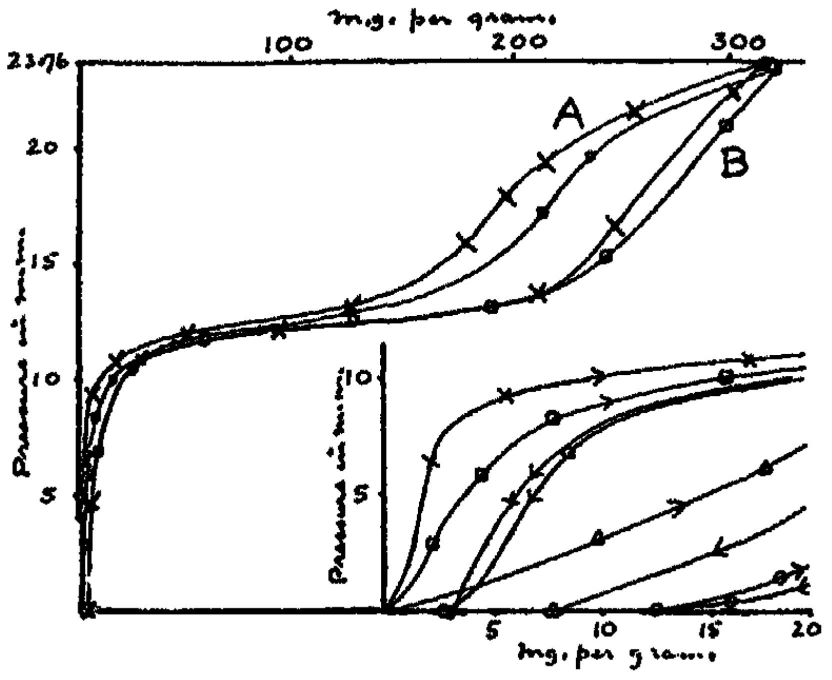

FIG. 3

(d) *Charcoal A—Twice Extracted with Alkali at one Atmosphere Pressure—Evacuated at 800°C.*

(i) Time not recorded.

(ii) 2.75 m.g./gram.

(iii) Not determined.

(iv). See Fig. 3B. Fig. 3 also contains, plotted on a larger scale, the detail of the isotherms at small q values for both once and twice alkali-extracted charcoals, for unextracted charcoal (triangles; see Part IV, Fig. 1B), and for a specimen which had been previously saturated with water vapour (circles; see Fig. 7).

(e) *Charcoal A—Extracted by Alkali at Three Atmospheres Pressure—Evacuated at 800°C.*

(i) Time not recorded.
(ii) Not determined.
(iii) Not determined.
(iv) See Fig. 4, which contains the isothermals at low q values of all the alkali-extracted specimens of Charcoal A, together with the corresponding data for the unextracted charcoal. Three points only were determined, on the sorption bunch.

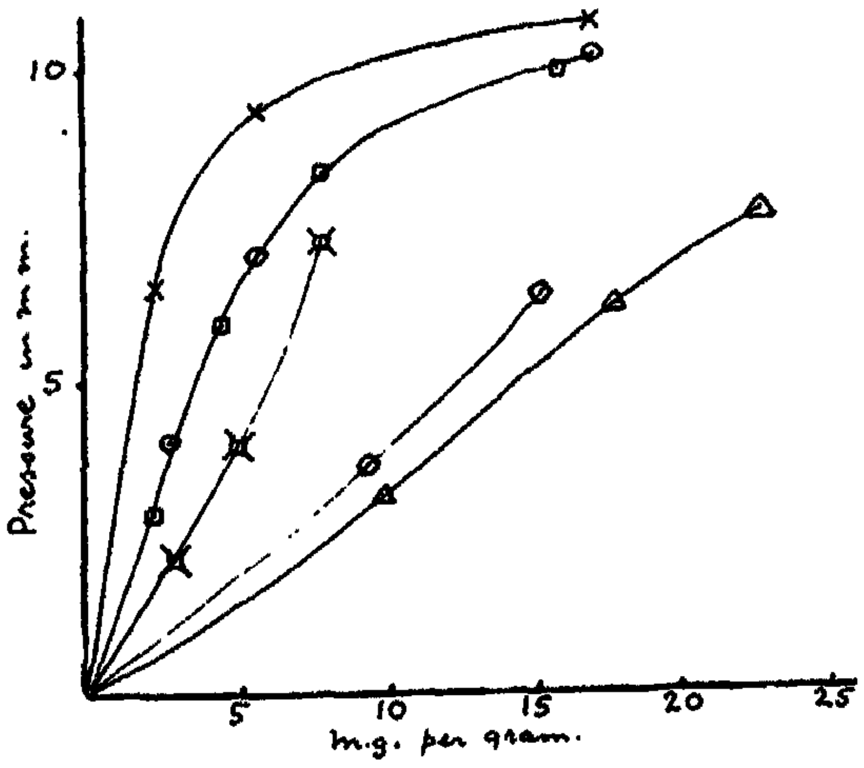

FIG. 4

△ Unextracted
× One extraction —one atmosphere
□ Two extractions—one atmosphere
○ One extraction —three atmospheres
⊠ One extraction —4-8 atmospheres
◇ One extraction —10 atmospheres

(f) *Charcoal A—Extracted by Alkali at 4-8 Atmospheres Pressure—Evacuated at 800°C.*

(i) Time not recorded.
(ii) Not determined.
(iii) Not determined.
(iv) See Fig. 4. Three sorption points were determined.

(g) *Charcoal A—Extracted by Alkali at 10 Atmospheres Pressure—Evacuated at 800°C.*

(i) Time not recorded.
(ii) Not determined.
(iii) Not determined.
(iv) See Fig. 4. Two points only were determined on the sorption branch.

4. Discussion

The salient features of the effects of a single alkali extraction will be obvious from a comparison of Figs. 1-3 with Figs. 1-3 of Part IV. In every case the following statements hold. (1) There is a marked diminution in the sorptive capacity of the charcoal at the lowest pressures, the curves for the extracted charcoals rising far more steeply from the origin. (2) The pressure at which the isothermal begins rapidly to turn over, prior to becoming concave to the pressure axis, is higher for the extracted charcoal, the effect being similar qualitatively to that of raising the outgassing temperature from 270° to 800°. (3) The course of the isothermal at intermediate pressures, more particularly on its desorption branch, tends to be flatter for the extracted charcoal, and the isothermal in general lies at higher pressures. (4) The quantity of water retained at zero pressure is less for the extracted charcoal. (5) The degree of hysteresis is, on the whole, not much affected.

In general, these changes are shown in their most pronounced form by Charcoal C, where the results are very remarkable, and to the least extent by Charcoal B. This difference in behaviour is very striking when the effect of extraction on the saturation figure is considered. In the case of Charcoal C, there is a considerable diminution, accompanied by a change in form of the isotherm near saturation, but Charcoal B actually shows a slight increase in saturation capacity. Charcoal A, if comparison be made with Fig. 1B of Part IV, hardly shows any change in saturation value, but if Fig. 7 of this paper be used instead (and we shall see that there is justification for this course), then the effect of extraction is seen to be to cause a definite decrease, though less pronounced than with Charcoal C. Comparison with Fig. 7 of this paper indeed indicates the effect of alkali extraction on Charcoal A to be greater in every respect than would be gathered from comparison with Fig. 1B of Part IV.

A comparison with the effects of HCl extraction on the isothermals of "270° C." A and B charcoals shows the action of the alkali to have been more profound than that of the acid, particularly in the intermediate pressure region of the isothermal, where the acid extraction has hardly made any difference. The ash content of the alkali and the acid extracted charcoals, both A and B, is almost identical. Unfortunately, no comparison is possible in the case of Charcoal C, where the only isothermal measured for the "270°C." acid-extracted charcoal was determined in a nitrogen stream (Part III, Fig. 3A).

It remains to consider the effect of a second extraction, and of extraction at higher pressures, as exhibited in Figs. 3 and 4. This effect can be expressed by saying that further treatment with alkali appears to re-activate the charcoal. The desorption branch of Fig. 3B is practically identical with that of Fig. 3a at intermediate and low pressures, but the complete sorption curve and the high pressure portion of the desorption curve are both displaced in the direction of increased q values. Fig. 4 shows that a single extraction at three atmospheres gives a charcoal with an isothermal practically identical with that of the charcoal twice extracted at one atmosphere. Alkali treatment at higher pressures results in a further displacement of the curves in the direction of greater sorption—indeed, the isothermal for the charcoal extracted at ten atmospheres is very near that of the original unextracted charcoal. At one time, we were inclined to think that this displacement of the isothermal was due to absorption of water by alkali which had been forced into the innermost recesses of the charcoal under the high pressure used, and had not been removed by the subsequent extraction with HCl and water.[1] Further reflection, however, bearing in mind, in particular the thorough desublimation at 800° to which these charcoals were subjected before water vapour was admitted, suggests that our former idea was incorrect, and that the increased sorptive power is due, not to the presence of adventitious alkali, but to a real reactivation of the charcoal itself.

B. RESORPTION—LAG OR DRIFT—HYSTERESIS

5. Introductory

In all our experiments so far described, whether done in a gas-stream or under "static" conditions, we found a greater or lesser degree of hysteresis, *i.e.* the sorption and desorption curves did not coincide, the latter always being displaced in the direction of lower pressures or higher *q* values. Obviously closely connected with this phenomenon is the fact that equilibrium, or apparent equilibrium, was slowly reached, marked "lag" or "drift" being observed. In actual point of time required to pass from one point on an isothermal to another, this was most noticeable at intermediate pressures, but if the quantity of water vapour sorbed be taken into account, this difference would seem to disappear, at all events when working in a gas-stream (Part III, Fig. 1). When using the static technique, it is more difficult to come to any conclusion on the matter.

The general opinion of previous workers on the sorption of vapours, whether on charcoal or silica gel, is that the true equilibrium curve is the desorption curve. Those authors who hold the capillary condensation theory attribute the lag in the determination of the sorption curve to the difficulty of wetting the capillary walls during the sorption process.[2] This difficulty is due to the presence of air,[3] and if this is completely removed, sorption and desorption curves on silica gel coincide,[4] except in the case of water. Coolidge, using the static technique, attributes hysteresis in the majority of cases to the accumulation of displaced gases in the vapour phase during sorption, with consequential false pressure readings.[5] In his later

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[1] Part I, p. 454. The presence of such firmly retained alkali was merely assumed and never demonstrated experimentally.

[2] E. G., Anderson: Z. physik. Chem., 88, 191 (1914).

[3] Gustaver: Kolloidchem. Beihefte, 15, 185 (1922); Katz: Proc. Amsterdam Acad., 26, 548 (1923).

[4] Patrick: Kolloid-Z., 36, (Ergänzungs-Band), 272 (1925).

[5] J. Am. Chem. Soc., 46, 596 (1924).

work,[1] he adopts a modified point of view and, in the particular case of water on charcoal, is inclined to ascribe hysteresis very largely to the presence of inorganic ash constituents which sorb water preferentially.

6. Experimental

We have carried out a number of experiments bearing on these points, which will now be described. In all cases, the static technique was used. Early in our work, we observed that the quantity of water vapour taken up during sorption at low pressures appeared to depend on the rate of admission of water vapour to the apparatus. The first observation was made after determining the isothermal at 15°C. for Charcoal A (see Part IV, Fig. 7). At the conclusion of the experiment, the charcoal was outgassed, and water vapour again admitted up to a maximum pressure of 3.94 m.m., but with smaller charging pressures, *i.e.*, more gradually than before. The results, together with those obtained previously, are plotted in Fig. 5. The effect of the lower charging pressure in decreasing the efficiency of sorption[2] is seen to be quite definite.

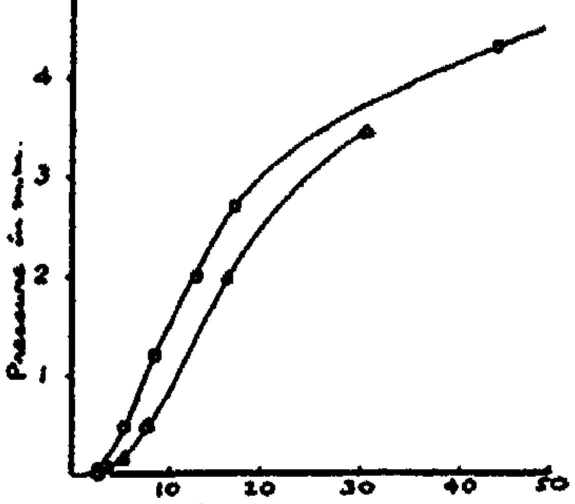

Fig. 5

☐ Normal Method of sorption
△ Gradual admittance of vapour

Following on this, some experiments were done which indicated that, whilst a rise in outgassing temperature from 270° to 600° increased the quantity of water vapour taken up at those low pressures, a further increase in outgassing temperature to 800° had rather the opposite effect. On the other hand, whilst the water thus sorbed by a "600° C." charcoal was as readily given up on outgassing as by a "270°C." charcoal, the charcoal outgassed at 800° gave up its water with difficulty. To investigate this point further, a systematic series of experiments was carried out on a specimen of Charcoal A after outgassing at 780°. Water vapour was gradually admitted at 15°C. until a pressure of the order of 4.5 m.m. had been reached, the charcoal then being desorbed in stages, and its evacuated weight at zero pressure determined. This sorption-desorption cycle was carried out four times successively on the same specimen of charcoal. After the second sorption point in the fifth cycle had been determined, an accidental air-leak occurred, following on which the charcoal was finally evacuated at 15° and weighed. The total increases in weight after the "zero" pressure evacuation at the end of each cycle are given in Table I, and the results of the whole experiment exhibited in Fig. 6A, where sorption curves are shown by continuous, and desorption curves by dotted, lines.

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[1] J. Am. Chem. Soc., 49, 708 (1927).

[2] Cf. Lemon and Blodgett: Phys. Rev., (2) 14, 394 (1919).

TABLE I

Cycle	Total increase in weight in m.g./gram	Cycle	Total increase in weight in m.g./gram
1	5.70	4	10.72
2	7.37	5	10.72
3	9.05		

Subsequent outgassing (finally at 800°) resulted in the recovery of 7.16 m.g./gram of water and of evolved gases amounting to

C O 1.7 m.g./gram
C O_2 0.69
H_2 0.24
N_2 0.46

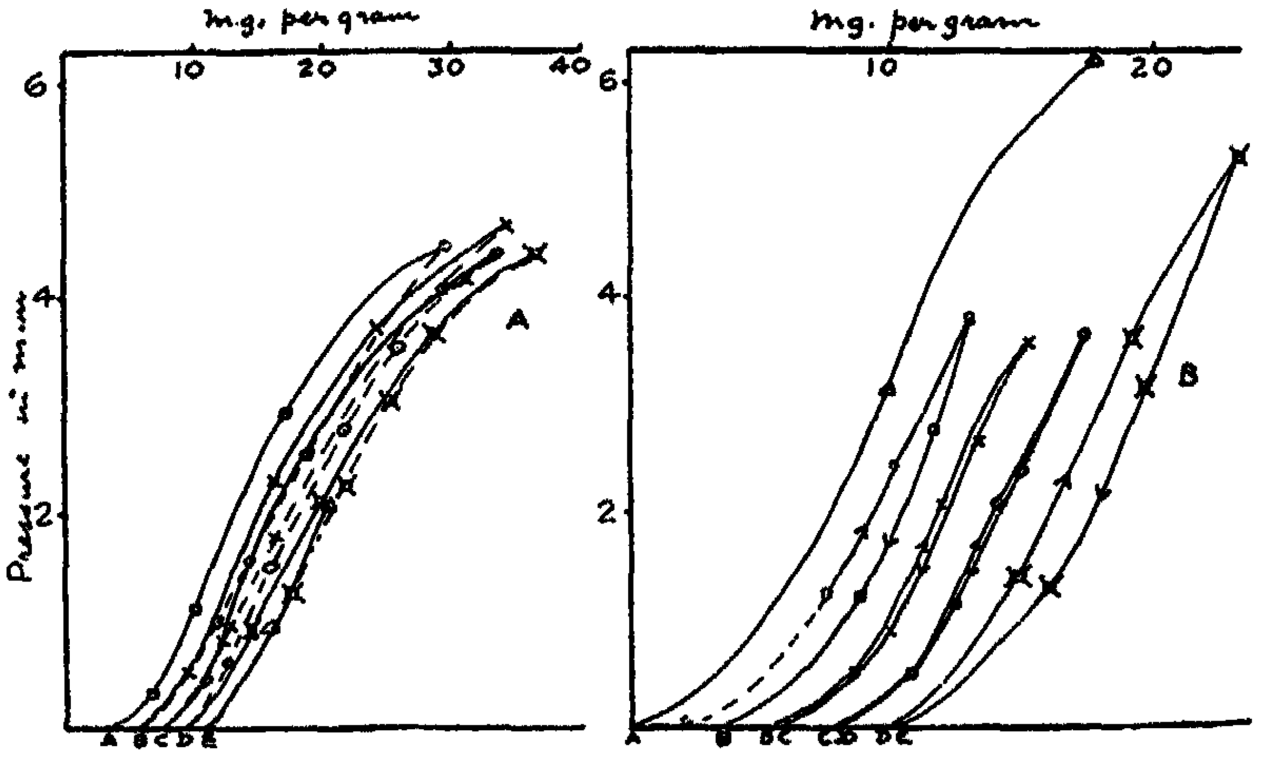

FIG. 6

Series 1. A □ B
2. B × C
3. C ○ D
4. D ⧗ E
5. E △ E

Series 1. A □ B
2. B × C
3. C ○ D
4. D ⧗ E

Attention is drawn to the following points. In Cycles 2, 3 and 4, the increments in the quantity of fixed water are practically identical, viz., 1.67, 1.68 and 1.67 m.g./gram respectively. The general tendency of the resorption curves seems to be to coincide initially with the previous desorption curve, and then to rise more steeply, passing into the previous hysteresis loop. The hysteresis loops themselves tend to become narrower in the higher pressure region as the experiment proceeds. Finally, the incomplete Cycle 5, where the maximum pressure reached only 2.09 m.m., caused no further increase in weight of the charcoal after its final evacuation at 15°.

This last fact suggested that, just as a high charging pressure was associated with "lag" in the sorption curve, so also it tended to produce a desorption curve lying at high q values, both effects of course increasing the size of the hysteretic loop. Another series of experiments similar to the above was accordingly done. Charcoal A, outgassed at 800°, was again employed. It was used at 25°, not at 15°, in order that the results might be compared with those of the main body of our work. And the relative pressure of water vapour to which it was exposed was at first kept lower than in the above experiment, a value of 3.80 m.m. ($P/p_0 = 0.160$) not being exceeded, whereas in the previous series at 15°, the maximum pressure of 4.67 m.m. corresponded to a relative pressure of 0.365. The results are plotted in Fig. 6b. In order to make them clearer, each successive hysteretic loop is displaced to the right by an amount equivalent to a q value of 2 m.g./gram. It will be seen that, whereas Cycle 1 exhibits considerable hysteresis, this is far less in Cycle 2, and in Cycle 3 has almost disappeared. The points B, C and D correspond to 3.55, 3.88 and 4.02 m.g./gram of water vapour respectively. Not only had considerably less water been found in Cycle 1 as compared with Cycle 1 of Fig. 6a, but the increments found in succeeding cycles are far smaller than those held in the corresponding cycles of the 15°C. experiments. Finally, in order to test the point further, a last cycle was investigated in which the maximum pressure was allowed to rise to 5.33 m.m. ($P/p_0 = 0.224$). This had the expected result of giving at once a far larger hysteresis loop, but on the other hand only a very small increase in "bound" water (from 4.02 to 4.20 m.g./gram).

TABLE II

q in m.g./gram at $p/p_0 = 0.1$

Temperature of Experiment	"270° C." Charcoal		'800° C." Charcoal	
	Low charging pressure	High charging pressure	Low charging pressure	High charging pressure
15°	12.5	8.9	10.2	—
25°	—	8.9	10.1	8.5

It is further of interest to note that the sorption branches of Cycle 1 at 15° and at 25° are practically identical if referred to the same relative pressure (compare Part IV, Fig. 8). For example, the q values at $P/p_0 = 0.1$ are respectively 10.2 and 10.1 m.g./gram at 15° and 25°, the corresponding figures for $p/p_0 = 0.15$ being 12.6 and 12.7 m.g./gram. Fig. 6B also has plotted on it the first two points of the sorption isothermal for "800°C." Charcoal A, determined by the static technique employed in our early experiments (water vapour admitted to the charcoal at a comparatively high pressure). The curve is seen to lie to the left of the first hysteresis loop.

In the following table are collected, from Fig. 8 of Part IV and Figs. 5 5 and 6 of the present paper, our data for the q values of the sorption isothermal of Charcoal A, all for a relative pressure of 0.1, but otherwise holding for two different outgassing temperatures, two different experimental temperatures, and two different methods of introducing the water vapour (gradual and sudden).

Although there are gaps in the table, the effects of the three variable factors are all clearly visible.

The above experiments, when considered in conjunction with the fact that the same "800°C." Charcoal A, after being taken up to 22.10 m.m., subsequently retained 7.67 m.g./gram at "zero" pressure and 25° (Part IV, Table II), suggested that the amount of "bound" water was a function of the pressure to which the charcoal had been exposed. On the other hand, this last figure had been exceeded by nearly 1 m.g./gram in experiments (not described here) similar to those illustrated in Fig. 6, in which the maximum pressure to which the charcoal had been exposed at 25° was only 5.70 m.m. As, moreover, the 22.10 m.m. of the Part IV experiment referred to was appreciably below the saturation figure (23.76 m.m.), and as the extrapolated saturation value for q of 320 m.g./gram (Part IV, Table II) appeared suspiciously low, it was decided to determine whether another complete isothermal for Charcoal A, outgassed at 800°C., and at the samt time to study the effect of resorption at intermediate and higher pressures. Further, in order to eliminate as far as possible the effect of "drift," in as far as this might be supposed to be due to slow movement of water into the innermost pores of the charcoal, it was decided to commence with charcoal saturated with liquid water, the desorption branch of the isothermal being thus obtained first. It was hoped that the saturation figure obtained in this way would be better defined than those found for this charcoal when starting with low aqueous vapour pressures, and it was further thought possible that the subsequent resorption curve might coincide with the desorption curve, *i.e.*, that hysteresis might disappear.

A specimen of Charcoal A was accordingly outgassed for five hours and then treated as follows:—

(i) with the container immersed in ice, water vapour at 14 m.m. pressure was allowed to distil on to the charcoal for 17 hours;

(ii) the closed container was immersed in boiling water for 10 minutes;[1]

(iii) the container was again immersed in ice for 7 hours;

(iv) the container was kept at 15°C. for 110 hours.

The quantity of water in and on the charcoal at this stage was 1100 m.g./gram. Desorption at 25° was then commenced, the pressure over the charcoal remaining at 23.76 m.m. for a considerable time. The first measured desorption point was 22.88 m.m., and the subsequent procedure was as follows:—

(a) desorption isothermal down to "zero" pressure—water retained 12.42 m.g./gram;

(b) resorption isothermal up to saturation—$q = 373.0$ m.g./gram;

(c) desorption down to 8.61 m.m.;

(d) resorption to saturation—$q = 377.6$ m.g./gram;

(e) desorption (four points only) down to "zero" pressure—water retained 12.06 m.g./gram.

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[1] In "annealing" in this manner, we were adopting procedure first used by Coolidge: *loc. cit.* (1924).

Throughout, equilibrium was reached far more rapidly than in other experiments, indicating that "drift" had been largley eliminated by the modified charging process. The charcoal was finally outgassed, first at 270°, then at 800°C. At the former temperature, 6.07 m.g./gram of water were recovered and, at 800°, a quantity of gas equivalent to

CO	1.6 m.g./gram
CO_2	0.20
N_2	0.27
H_2	0.07

The results of this experiment are plotted in Fig. 7, from which the following conclusions can be drawn.

(1) The figures, both for the saturation value of q and for the water held at "zero" pressure are well defined and not appreciably altered as a result of intervening desorption and resorption. (2) The desorption branch of the isothermal shows a certain instability at high pressures, but in its middle and lower reaches tends to give a curve on which all desorption points fall. (3) Quite definitely the sorption and desorption isothermals do not coincide. The sorption curve of Series I lies above the desorption curve from the very start, and the sorption curve of Series II soon, if not immediately, passes into the hysteresis loop and strikes the first sorption curve. (4) The sorption branch of Series II lies throughout close to that of Series I, but at slightly higher q values than the latter. (5) A comparison with Fig. 1 of Part IV shows that both sorption and desorption curves lie throughout at higher q (lower p) values than those of the corresponding curves of the isothermal for the same charcoal as determined by the usual technique. Of the above results, the fact that the amount of water retained at zero pressure is not

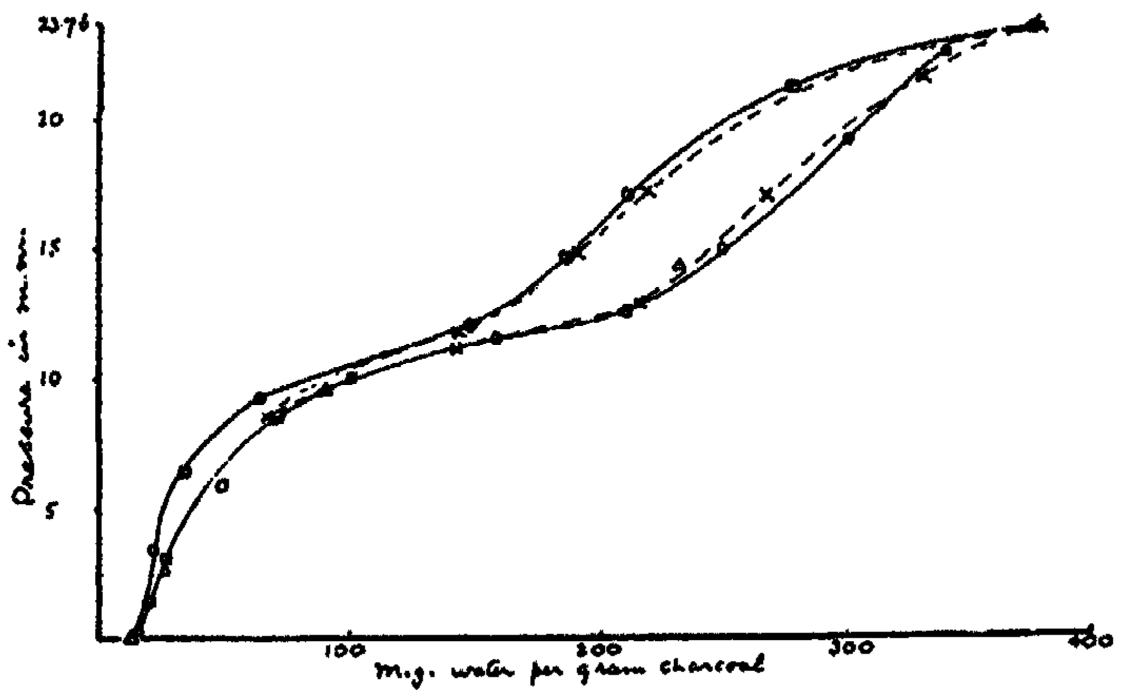

Fig. 7

Series I □
Series II ×
Series III △

affected by another resorption and desorption cycle and the demonstration of the very sharp difference between the sorption and the desorption curves are those which most concern us at the moment.

In order to test the same points with another charcoal, "800° C." Charcoal C, which had been put through the usual complete sorption-desorption cycle, was taken through a second similar complete cycle. Details of procedure are described under Experiment *f* of Part IV, and the results plotted in Fig. 8 (triangles), where the complete first cycle is shown by the dotted curve in Fig. 8A, and its low pressure points by the squares in Fig. 8B. Most of the results resemble those of the last experiment (Fig. 7)—thus, saturation and "zero" pressure figures are practically unaltered by the second treatment; the resorption curve on the whole tends to coincide with the first sorption rather than with the first desorption curve; both the second cycle curves tend to fall, during part of their course, within the first cycle hysteretic loop. There is, however, one qualitative difference, which is that, at low pressures, the resorption points fall very nearly, if not actually, on the desorption curve. In Fig. 8A, the resorption curve is drawn as falling within the hysteretic loop from the outset; in Fig. 8B, the first two points at 1.85 and 5.79 m.m. pressure are shown as coinciding with the desorption curve within the limit of experimental error. Our measurements are insufficiently accurate to say whether the coincidence is a real one. But it is certain that, if different, the two curves are far closer together than is the case in Fig. 7; and it is also certain that, if coincident, they must separate from one another at a pressure which can be only a very little higher.

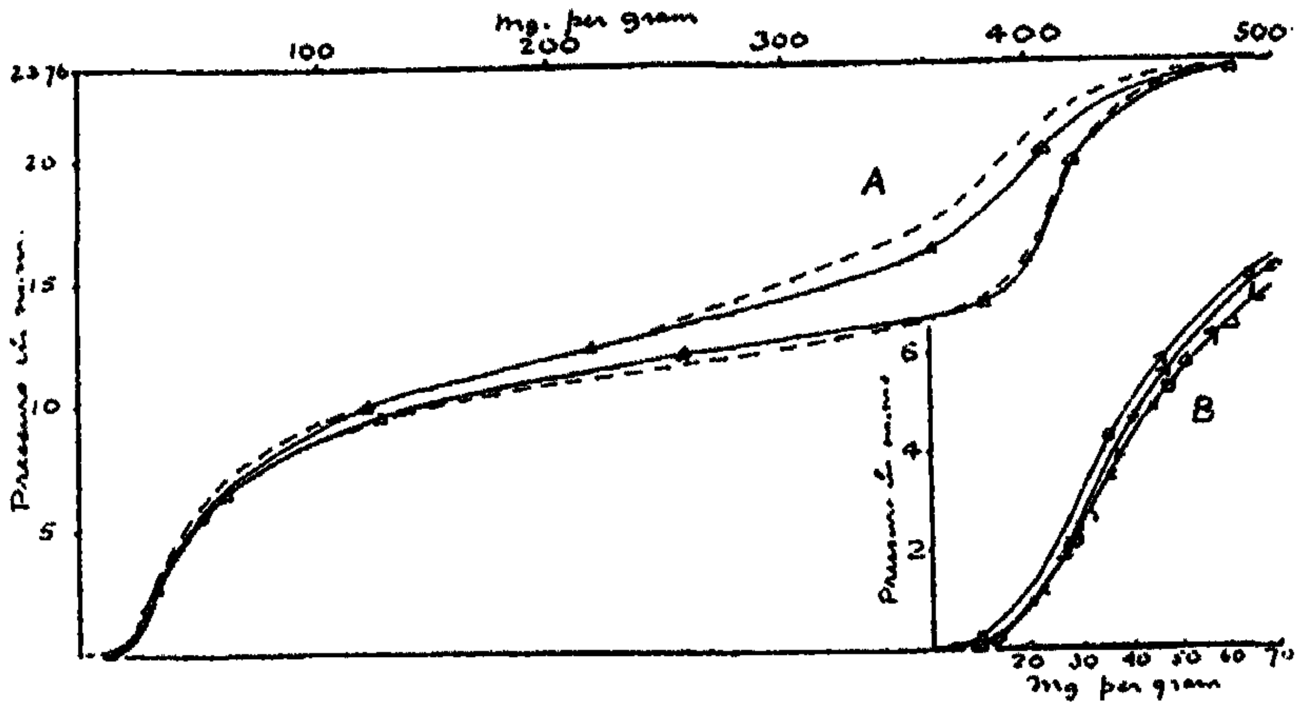

Fig. 8

Series I □
Series II △
Series III ×
Duplicate sorption ○

The resorption data obtained with Charcoal C, outgassed at 800° after extraction with alkali (see Section 3, Experiment (b), and Fig. 2) may conveniently be considered at this stage. Here the resorption curve of Series 2 quite definitely coincided with the first desorption curve up to about 7 m.m., then crossed the first hysteretic loop, and continued coincident with or just below the first sorption curve up to its maximum pressure of 16.02 m.m. Desorption from this point did *not* result in a sudden drop to the original desorption curve, as would have been the case if Coolidge's original view of hysteresis were correct, but in a smooth and normal descent to the latter. Series 3 only consisted of four points, but each of them gave a result of interest. Resorption, this time commencing from a point on the flat intermediate pressure portion of the desorption isothermal, resulted in a curve which crossed the hysteretic loop as before, and then proceeded along inside it to a point definitely below the original sorption curve at 16.78 m.m. When equilibrium had been reached at this pressure, the charcoal was desorbed by exposing it, not to the evacuated apparatus, as was usual, but to an aqueous vapour pressure corresponding closely to that on the original desorption curve for the same q value (13.8 m.m.). The result was merely a slight desorption and fall in pressure to 16.53 m.m., with no tendency whatever to drop to the original desorption curve. Finally, the charcoal was outgassed at 25°, and the weight of bound water found to be almost identical with that obtained after the first complete cycle.

Alkali-extracted "800°C." Charcoal C therefore behaves quite similarly in the matter of resorption and hysteresis to the unextracted charcoal, and the main difference between Charcoals C and A would seem to be that a resorption curve tends to leave the typical desorption curve in order to cross the hysteretic loop sooner, *i.e.*, at lower pressures, in the latter case than in the former. A few other scattered observations made by us confirm this. In Fig. 5 of Part IV are plotted two resorption points determined on acid-extracted "270°C." Charcoal A at the close of the sorption-desorption cycle. Their pressures were 3.77 and 4.25 m.m. respectively, and they apparently fall within the hysteretic loop. Fig. 3C of Part IV contains, plotted as triangles, three resorption points (maximum pressure 4.26 m.m) determined after the completion of the isotherm for "270°C." Charcoal C. They clearly fall on the desorption curve, as also do the eight resorption and desorption points (maximum pressure 4.82 m.m.) of Series 3, measured on "800°C." Charcoal C at the conclusion of the second complete sorption-desorption cycle (Fig. 8 of this paper, and Experiment (f) of Part IV).

7. Discussion

The experimental conclusions to be drawn from the above work can be summarised as follows.

(1) Using a freshly outgassed specimen of charcoal, the sorption and desorption curves are distinct throughout, the only exception being provided by Charcoal J (sugar charcoal) at pressures near saturation.

(2) This hysteresis is real, and not merely due to false measured pressures caused by the accumulation in the vapour phase of gases expelled from the charcoal.

(3) A second complete sorption (complete resorption) curve tends at low pressures to remain initially on the desorption curve (over a measurable pressure range, perhaps 6 m.m., in the case of Charcoal C, to an imperceptible degree with Charcoal A). It then crosses the initial hysteretic loop until it reaches, or nearly reaches, the sorption curve, and follows the general course of the latter, falling below it to a greater extent as the pressure rises. The final saturation value is the same as, or a little greater than, that of the original sorption curve.

(4) If resorption be commenced from a point on the original desorption isothermal, the curve crosses the hysteretic loop and tends to coincide with the course it would have taken if it had started out from zero pressure.

(5) A second complete desorption (complete re-desorption) curve tends to run along or very near to the original desorption curve. This coincidence is exact at low pressures; at intermediate and higher pressures a tendency is observed for the redesorption to lie above the desorption curve. The effect —a diminution in the size of the hysteretic loop—is in the same direction as that observed under (3), but less important than the latter. The final amount of water vapour left in at "zero" pressure is practically the same as that found after the original desorption isotherm.

(6) If re-desorption be commenced from a point on the resorption isothermal, the curve crosses the hysteretic loop, and tends to coincide with the course it would have taken if it had started out from saturation pressure.

(7) Using a fresh specimen of Charcoal A, a low *charging* pressure (gradual admission of water vapour) increases the q values on the low pressure point of the sorption curve.

(8) If Charcoal A is originally saturated with water vapour and "annealed," subsequent "drift" is largely eliminated.

(9) At the end of a single *partial* sorption-desorption cycle on Charcoal A, the amount of water vapour left in at zero pressure depends on the maximum relative pressure value of the final sorption equilibrium point (or possibly on the actual non-equilibrium charging pressure used?), being greater, the higher the latter.

(10) If Charcoal A be put through a series of resorption-desorption cycles, the maximum sorption p/p_0 value being kept low and constant, the degree of hysteresis, as measured by the area of the hysteretic loop, steadily diminishes. This diminution chiefly affects the higher pressure portion of the loop. Each cycle up to a point results in an increment in the amount of water held at "zero" pressure at the end of the cycle. This increment is greater, the higher the maximum p/p_0 value.

Very few previous observations have been published on re-sorption phenomena with water on charcoal. Bachmann,[1] working with coconut charcoal, found the resorption curve to strike up inside the first (very large) hysteresis loop, then to cross over and coincide with the desorption curve over a short pressure range, once again to rise into the first hysteresis loop and finally

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[1] Z. anorg. Chem., **100**, 1 (1917).

to regain the original sorption and desorption curves at the saturation point. There were thus two separate hysteresis loops contained between the desorption and the resorption curves. Rakovsky,[1] employing a simple technique and working in presence of air, used a number of charcoals, taking them up to saturation at 19°C. and determining at least one complete resorption cycle. In the case of Kahlbaum sugar charcoal, the resorption curve lay very near to the desorption curve throughout, finally finishing at a higher saturation value. The redesorption curve exhibited very slight hysteresis, about six per cent additional water being held at the end of the resorption cycle.

A blood charcoal of Russian origin, previously extracted with H_2SO_4, gave a resorption curve which, like our own, crossed the hysteresis loop on to the sorption curve. The re-desorption curve coincided with the first desorption curve over the greater part of its length, but finished by diverging at low pressures in the direction of considerably augmented hysteresis, the amount of water held at "zero" pressure being increased by nearly forty per cent. Kahlbaum blood charcoal behaved similarly, but in this case the increment in the quantity of "bound" water as the result of the resorption cycle was far greater—100 per cent. Further resorption and redesorption resulted in no change.

These results, particularly in the matter of the increase in "bound" water following on a second complete sorption cycle, are not all in agreement with our own, but differences in nature of charcoal and of experimental technique may well account for this.

8. Recovery of Bound Water by High Temperature Evacuation

Before concluding our survey of the experimental work, it will be convenient to consider the data concerning the recovery, by high temperature evacuation, of water which is so firmly held after the desorption process as not to be given up by exposure to zero water vapour pressure at the experimental temperature. Tables III and IV include all available data obtained on this subject; unfortunately in many of the later static experiments this particular determination was omitted.

The figures obtained for the "270°C." and "800°C." Charcoal A in the air stream have been omitted, the former because the conditions under which the charcoal was exposed to saturated water vapour were ill-defined, there being a strong probability that liquid actually condensed in the charcoal tube, the latter because of an accident having happened to the apparatus at a moment before probably even the outgassing at 270° was complete.

The chief conclusions to be drawn from these tables are the following.

(1) The amounts of water held at zero aqueous vapour pressure and 25° are far greater in the dynamic than in the static experiments. The conditions in the former are certainly less exactly defined, owing to the existence of displacement effects and the possibility, the the air stream experiments, of slow

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[1] J. Russ. Phys. Chem. Soc., 49, 371 (1917).

TABLE III
Static Technique

Charcoal	Outgassing temperature	Conditions	Maximum sorption pressure (in m.m.)	Water bound at 25°C. (in m.g./gram)	Water recovered by outgassing (in m.g./gram)	Water not recovered by outgassing (in m.g./gram)
A	270°	Unextd.	22.68	4.28	3.98	0.30
A	800°	Unextd.	6.61	4.52	4.48	0.04
A	800°	Unextd.	22.10	7.67	5.25	2.42
A	800°	Unextd.	23.76 (saturated at commencement)	12.06	6.07	5.99
B	270°	Unextd.	23.76	4.50	2.91	1.59
B	270°	HCl extd.	23.76	2.32	2.32	0.00
C	270°	Unextd.	23.47	5.74	5.09	0.65
C	800°	Unextd.	23.44 (twice)	9.92	8.86	1.06
C	800°	Alkali extd.	23.76	1.58	0.91	0.67
J	110°	HF extd.	23.25	5.35	1.86	3.49
A	800°	Unextd.	4.67 (at 15°—four times above 4.4 m.m.)	At 15°C. 10.72	7.16	3.56

fixation of oxygen during the determination of the isothermals. These factors, however, can certainly not completely account for the differences observed.

(2) On the other hand, the figures for water recovered by outgassing at a higher temperature are of the same order, usually higher in the dynamic experiments, but in two cases higher in the static experiments.

(3) It follows that the differences noted under (1) reappear when the quantities of water irrecoverable by high temperature evacuation are considered.

(4) The effect noted under (3) may be caused by the actual presence of the stream of gas in the dynamic experiments or, more probably, by the very long duration of those experiments. This last suggestion receives some support from the comparatively large quantity of water vapour held at high temperatures by "800°C." Charcoal A which had initially been saturated with water vapour and then "annealed" and allowed to stand before commencing the determination of the isothermal—also for the results at 15° with the same charcoal (several cycles).

TABLE IV

Dynamic Technique

Charcoal	Outgassing temperature	Conditions	Nature of gas stream	Maximum sorption pressure (in m.m.)	Water bound at 25°C. (in m.g./gram)	Water recovered by outgassing (in m.g./gram)	Water not recovered by outgassing (in m.g./gram)
A	270°	Unextd.	N_2	20.06	12.6	5.9	6.7
A	800°	Unextd.	N_2	23.76	43.5	9.7	33.8
B	270°	Unextd.	Air	23.76	12.2	4.8	7.4
C	270°	Unextd.	Air	23.76	9.8	2.8	7.0
C	270°	HCl extd.	N_2	23.76	13.7	4.7	9.0
C	800°	Unextd.	Air	23.76	22.7	7.2	15.6
C	800°	Unextd.	N_2	23.76	40.0	9.2	30.8

(5) Water is more completely recoverable by high temperature evacuation (a) from a "270°C." than from an "800°C." charcoal; (b) from an extracted than from an unextracted charcoal (the determination of the isothermal on "270°C." HCl-extracted Charcoal C in a N_2-stream took 300 hours longer than the corresponding determination for the unextracted charcoal in an air stream); (c) if the charcoal has been exposed to a low charging pressure.

(6) Reference to the accounts of the experimental work will show that, in the great majority of cases, it is quite impossible to account for the missing water on the assumption that, in outgassing, it has been evolved in the form of H_2, CO and CO_2, *i.e.*, that the water-gas reaction has taken place between it and the charcoal, although this is doubtless the explanation in all cases of a part of the deficiency. We are led to the probable conclusion that charcoal, after saturation with water, can retain appreciable quantities of the latter even after outgassing at temperatures up to 800°C.

We have hitherto done no further work to test this last conclusion, but it receives support from some experiments by Rakovsky.[1] A specimen of Kahlbaum blood charcoal, dried over concentrated sulphuric acid, lost 3.32 per cent by weight of water when ignited at a red heat in a current of oxygen, the water collected was 9.70 per cent of the initial weight of charcoal. Another specimen of the same charcoal, first dried over concentrated sulphuric acid, was twice taken through a complete sorption-desorption cycle, at the conclusion of which it showed a definite increase in weight of 8.8 per cent after standing again at the temperature of the experiment over concentrated sulphuric acid. When a specimen of the charcoal in this condition was heated to redness in nitrogen, it lost 6.81 per cent by weight of water; when burnt in a current of oxygen, the water collected was 16.53 per cent of the weight taken, whereas 17.0 per cent *i.e.* $\frac{(9{\cdot}7 + 8{\cdot}8)100}{108{\cdot}8}$ would have been anticipated from the previous data. Even if it be held that the original charcoal specimen contained no more water than was represented by the 3.32 per cent lost in the nitrogen stream, the second result can only be explained on the assumption that, in the course of the two sorption cycles, the charcoal had taken up four per cent of its weight of water so firmly as to retain it at a red heat in a nitrogen stream.

The experimental data comprised in Parts II-V of this series will be correlated and discussed in Part VI.

University of London,
King's College,
May 28, 1929.

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[1] Loc. cit.

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THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION V. HYDROUS OXIDE-ALIZARIN LAKES

BY HARRY B. WEISER

In a recent investigation of the formation of hydrous oxide-alizarin lakes from sodium alizarate baths,[1] it was concluded that the lake formation process consists in an exchange adsorption of the dye anion with the less strongly adsorbed chloride or nitrate ion in the hydrous oxide and not to direct adsorption of neutral sodium alizarate as suggested by Bull and Adams[2] and by Williamson,[3] in Bancroft's laboratory. On adding sodium alizarate to positive sols of the hydrous oxides of iron, chromium, and aluminum stabilized by preferential adsorption of hydrogen ion, the color lakes were precipitated leaving most of the sodium in the supernatant solution as sodium chloride. It was thus tacitly assumed that the lakes formed as above described were hydrous oxide-alizarin acid adsorption complexes. Bancroft[4] questions the accuracy of this conclusion on the grounds that the alumina-alizarin lake was red and adsorption of the yellow orange alizarin acid would not be expected to give a red lake. The red color in the cases under consideration was attributed to ammonium alizarate formed as a result of the failure to remove ammonium completely from the hydrous oxide sols.

In this connection it should be recalled that the alkali and alkaline earth alizarates are dark purple in color. A thin film of sodium alizarate is purple both in transmitted and reflected light in marked contrast to the red color of the dilute solution or the bright red of the alumina-alizarin lake. The very weak alizarin acid is insoluble in water and the alcoholic solution possesses a yellow orange color similar to that of the solid crystals. Since the claret red color of dilute aqueous solutions of sodium alizarate is definitely associated with the anion, the problem presented is whether the color of the hydrous oxide-alizarin lakes is influenced to any marked degree by the cation accompanying the dye anion. In view of the fact that the earlier conclusions are open to question because of the probable presence of ammonium in the hydrous oxides, it seemed advisable to make some observations with a really pure alumina such as one might expect to get by the action of amalgamated aluminum on distilled water.[5] Such experiments served as the starting point in this investigation in spite of the claim[6] that a pure alumina does not form a lake with alizarin.

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[1] Weiser and Porter: J. Phys. Chem., 31, 1824 (1927).

[2] J. Phys. Chem., 25, 660 (1921).

[3] J. Phys. Chem., 28, 891 (1924).

[4] J. Phys. Chem., 32, 925 (1928).

[5] Cf. Bancroft: J. Phys. Chem., 32, 925 (1928).

[6] Liechti and Suida: J. Soc. Chem. Ind., 4, 587 (1885); Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 2, 574 (1916).

Experimental

I. Preparations

Alumina gel from amalgamated aluminum. An alumina free from alkali or ammonium was prepared by a modification of the method of Wislicenus[1] for preparing fibrous alumina. Five to ten grams of pure granular aluminum were treated with hydrochloric acid which was allowed to act until the surface of the metal was thoroughly cleaned. After washing, the granules were transferred to a pyrex flask and shaken with 100 cc of water containing a few drops of a saturated solution of mercuric chloride. The solution was then poured off and the metal was washed repeatedly by decantation until the wash water gave no test for chloride with silver nitrate. After adding 350 to 400 cc of water to the flask, it was stoppered lightly and allowed to stand several days, shaking at intervals. The reaction, which was fairly rapid at the outset, gradually subsided, so that several repetitions of the above operation were necessary to obtain a sufficient supply of alumina. The oxide was removed from the unattacked aluminum by decanting the suspension.

Sheet alumina may be substituted for the granular metal. The latter possesses the advantage of offering a larger reacting surface for a given mass but the former may be supported so that the oxide falls from the surface as it forms and so does not interfere with the progress of the reaction.

Since the amalgam retains a small amount of chloride, the oxide formed as described is not entirely free from chloride. Such a preparation may be obtained by amalgamating a carefully cleaned sheet of aluminum, washing to remove the excess of finely divided mercury and allowing to react vigorously with water for an hour or more, changing the water at intervals. This action cleans the surface of the aluminum thoroughly and thereafter the oxide is free from chloride as evidenced by the fact that a sample dissolved in nitric acid gives no test for chloride with silver nitrate.

Chloride-free oxide may be formed also with sheet aluminum thoroughly cleaned with carborundum paper and amalgamated with metallic mercury.

If the amalgamated aluminum is kept in moist air instead of being covered with water, voluminous filaments of so-called "grown" alumina are formed.

The oxide first formed in the presence of an excess of finely divided mercury will have a gray appearance and should be discarded. If the action is very rapid, in the absence of an excess of mercury, the resulting oxide is gray in color because of the presence of fine particles of aluminum. This coloration disappears on standing owing to reaction of the fine particles with water. When properly prepared, the oxide is pure white and quite finely divided. Cataphoresis experiments show the particles to possess a slight positive charge in contact with water but they settle out on standing.

Alumina sol from amalgamated aluminum. The failure of the finely divided oxide to form a stable sol under the conditions described in the preceding

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[1] Wislicenus and Kaufmann: Ber., 28, 1328 (1895); Wislicenus: Kolloid-Z., 2nd Supplement, XI (1908).

paragraph was due to the absence of electrolyte. For the purpose at hand a stable sol was obtained by adding two or three drops of hydrochloric acid to the water covering the amalgam. Under these conditions a considerable amount of the alumina remained suspended in the water due to sufficient positive charge resulting from preferential adsorption of hydrogen ion. The conditions were observed to favor a more rapid and prolonged action of the aluminum with the water.

Ferric oxide sol. Colloidal ferric oxide was prepared by hot dialysis of the sol formed by adding ferric chloride solution slowly to boiling water, according to the method of Sorum.[1]

Solutions. The calculated amount of Kahlbaum's pure resublimed alizarin required to make 250 cc of M/100 sodium alizarate was suspended in 50 cc of water which was heated and stirred until the water had displaced the air from the fine, loosely packed crystals. To this suspension was then added the exact amount of a sodium hydroxide solution prepared free from carbonate and chloride. By digesting over night the alizarin was converted completely into soidum alizarate and the solution was diluted to the required volume.

Saturated solutions of the alizarin in alcohol, ether, and carbon bisulfide were prepared and stored in pyrex vessels. Since alcohol frequently contains a small amount of alkali dissolved from the soft-glass containers,[2] only freshly distilled alcohol was employed.

II. OBSERVATIONS WITH ALUMINA

Alumina (from amalgamated aluminum) and sodium alizarate. Preliminary observations disclosed that the pure alumina suspended in water adsorbed but little alizarate. To 100 cc of a suspension containing 0.16 gram Al_2O_3 was added M/100 sodium alizarate solution dropwise until the clear supernatant solution showed a distinct pink color. But 0.75 cc of the solution was required. The particles of alumina possessed a slight positive charge which was further reduced by adsorption of a small amount of alizarate ion and the voluminous precipitate assumed a faint pink color. The supernatant liquid evaporated to a small volume, gave a very faint test for chloride, an amount which probably corresponded with the small amount of alizarate adsorbed.

Contrary to the above observations, Ackerman in Bancroft's laboratory reported at the Columbus Meeting of the American Chemical Society that he obtained a red lake with alumina from aluminum amalgamated in mercuric chloride solution. Since special precautions must be taken to prepare chloride-free alumina in this way, and since observations to be described later show that alizarate is taken up by alumina in exchange with chloride when the oxide is formed in the presence of chloride, I attributed the greater adsorption reported by Ackerman to the presence of more chloride in his preparations than in our own. While this may be true, I now know that it

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[1] J. Am. Chem. Soc., 50, 1263 (1928).

[2] Cf. Weiser and Radcliffe: J. Phys. Chem., 32, 1875 (1928).

is not necessarily the case. Thus it has been found that a chloride-free alumina will give a lake varying in color from red to a light pink depending upon the rate of formation and age of the sample. If the conditions are favorable for rapid action of the amalgam with the water, and the resulting alumina is treated with sodium alizarate a short time after it is formed, considerable adsorption takes place giving a red lake. On the other hand, if the oxide is allowed to age, the adsorption is so slight that only a pink lake results. The effect of the age and purity of the oxide on its capacity to adsorb alizarate is illustrated by the following experiments:

Two samples of alumina were prepared. In the first, special precautions were taken to avoid the presence of chloride and in the second, a small amount of sodium chloride was added to the water with which the alumina reacted. In both cases 5 cm × 8 cm amalgamated sheets were placed in 150 cc and allowed to react two hours. Fifteen cubic-centimeter samples of the suspended oxide were placed in test tubes and the change in adsorption capacity with time observed by adding a slight excess of M/100 sodium alizarate, centrifuging and noting the color of the lake. The results are given in Table I. The term age used in the table refers to the time between the preparation of the complete sample of oxide and the addition of the dye. It is evident that the chloride-free oxide loses its capacity to adsorb the dye more rapidly than the oxide containing adsorbed chloride.

TABLE I

Age of alumina	Color of Lake	
	Chloride-free alumina	Alumina containing adsorbed chloride
10 minutes	Dark red	Dark red
16 hours	Light red	Bright red
1 day	Light red	Bright red
2 days	Pink	Bright red
7 days	Light pink	Bright red

Alumina (from amalgamated aluminum) and alizarin. On adding an alcoholic solution of alizarin dropwise to 10 cc of the alumina suspension, a pink coloration was first observed which changed gradually on further additions, to a light brown and the precipitate was a yellowish brown. This might be mistaken for a brown lake but actually it proved to be merely a mixture of a light pink lake with yellow silky crystals of alizarin suspended in a solution more or less yellow orange in color depending on the amount of alcohol present.

On adding an alcoholic solution of alizarin to water, the insoluble acid separates in minute lustrous needles, the suspension possessing a yellowish, silky appearance. When the first drop of acid solution is added to the alumina a pink alumina-alizarin lake is formed. Further additions merely supply more of the silky alizarin crystals and yellow orange solution, the resulting mixture having a brown appearance. This conclusion was confirmed in a number of ways: (1) The brown mixture was thrown down with the centrifuge and subsequently treated with alcohol which dissolved the alizarin crystals leaving the pink lake. (2) The brown mixture was treated with sufficient dilute alkali to convert the alizarin to soluble alkali alizarate. On centrifuging the purple solution, most of the pink lake was thrown down. (3) A small amount of a suspension of the pink lake obtained in the above experiment with sodium alizarate, was mixed with a suitable amount of the fine suspension of alizarin in water. The resulting mixture appeared brown. (4) Microscopic examinations of a sample of the brown product made in the presence of as little alcohol as possible revealed the presence of the fine alizarin crystals mixed with the alumina. In settling, the pink hydrous alumina lake entangled the minute alizarin crystals in somewhat the same way that the alumina floc in water purification entangles and carries down the finely divided clay particles. (5) The presence of the fine alizarin crystals is unnecessary to give a brown preparation. Thus if the oxide suspension is centrifuged and the supernatant liquid replaced by alcohol, an alcoholic solution of alizarin may be added without precipitation of the acid. On shaking this mixture, a brown suspension resulted; but on centrifuging, a pink lake was thrown down and the clear supernatant liquid was the color of alcoholic alizarin solution.

It is obvious that the mixture would not possess the brown color observed if no lake formation took place with the resulting pink color. The actual color of the mixture will vary widely with the purity of the oxide and the relative amounts of the several constituents that are brought together.

If the pure newly formed oxide is suspended in alcohol and treated with an alcoholic solution of alizarin, a red lake is formed similar to that obtained with sodium alizarate.

Alumina sol (from amalgamated aluminum) and sodium alizarate. On adding an aqueous solution of sodium alizarate to the alumina sol prepared as above described, the sol was coagulated and the characteristic voluminous red alumina-alizarin lake was formed. Since the sol was free from alkali or ammonium ions it was of interest to know whether sodium ion was adsorbed in the lake formation process. To do this, sufficient alizarate solution was added to a portion of sol to cause complete coagulation. If too little alizarate was added, the coagulation of the sol was incomplete and the supernatant solution was colored; and if too much alizarate was added, the gel was repeptized. A measured portion of the clear colorless supernatant solution was evaporated to dryness in a platinum dish, the residue of chloride weighed, then converted to sulfate and weighed again. The results with two distinct sols are given in Table II. It will be seen that the alizarate ion is adsorbed in exchange with the chloride leaving sodium chloride in the solution.

It is of interest to note the much greater adsorption by this preparation than by the much purer oxide. In experiment 1 of Table II, the 90 cc of sol containing 0.216 gram of Al_2O_3, decolorized 25 cc of the M/100 sodium alizarate while 100 cc of a suspension containing 0.160 gram of the pure oxide did not decolorize 0.75 cc of the alizarate solution.

While the assumption has been made that the sols used in the above experiments are free from cations other than hydrogen, the possibility of the presence of aluminum ion in the sols has not been excluded. A sample of the ultrafiltrate obtained by ultrafiltratering the sol through a cellophane membrane under 10 atmospheres pressure, gave a slight precipitate of hydrous alumina on treating with ammonia. A similar precipitate was obtained on adding a small amount of sodium sulfate indicating that the aluminum which passed the ultrafilter was present as colloidal alumina and not as aluminum ion. To settle this question, two 50 cc samples of the ultrafiltrate were precipitated, the first with ammonia and the second with sodium sulfate. The alumina from the first sample weighed 0.0013 gram and from the second 0.0015 gram, showing conclusively that the ultrafiltrate was free from aluminum ion.

Table II

Substances mixed Sol	Sodium alizarate M/100 cc	Salt in 50 cc. weighed as NaCl	 Na_2SO_4	NaCl calculated	 observed	Na_2SO_4 calculated	 observed
90	25	0.0122	0.0153	0.0293	0.0281	0.0355	0.0352
		Salt in 75 cc weighed as NaCl	 Na_2SO_4				
80	28	0.0224	0.0291	0.0328	0.0322	0.0398	0.0419

The acid concentration of the ultrafiltrate was determined by titration with dilute standard alkali using phenolphthalein as indicator. A 50 cc sample was found to contain 0.002828 gram HCl corresponding to 0.05656 gram HCl per liter. Since this amount of chloride calculated as sodium chloride is but little more than one-fourth of the sodium chloride found in the supernatant solution in experiment 1 above, it follows that the alumina on the filter must contain most of the chloride, as the test proved.

While these experiments show the absence of aluminum ion in the intermicellar liquid and confirm the observation that an aged alumina is not attacked by dilute hydrochloric acid,[1] they do not exclude the possible presence on the oxide of some adsorbed aluminum ion formed by the action of the dilute acid on aluminum during the sol formation process. On the other hand, since a trace of HCl is found in the intermicellar liquid and since hydrogen ion is adsorbed by alumina more strongly than aluminum ion as evidenced by the stronger peptizing action of the former, than of the latter,[2] there is little doubt but that adsorbed hydrogen ion is the chief stabilizing ion in these sols.

Alumina sol (from amalgamated aluminum) and alizarin. The dropwise addition of an alcoholic solution of alizarin to 10 cc of the alumina sol gives

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[1] Cf. Weiser: "The Hydrous Oxides," 109 (1926).

[2] Weiser: J. Phys. Chem., 24, 521 (1920).

at once a pink lake which changes gradually to red. The red color develops quite rapidly on diluting the sol with alcohol so that the alizarin is not precipitated when added. The stability of the sol is not reduced sufficiently to agglomerate, the red lake remaining in colloidal solution indefinitely unless treated with a coagulating electrolyte.

Alumina gel (from $AlCl_3$) and sodium alizarate. While the absence of adsorbed aluminum ion in the alumina sols used in the preceding experiments has not been established, the following experiments show that adsorbed aluminum ion is unnecessary for the formation of the red lake. A five-gram sample of aluminum chloride was dissolved in a liter of water and precipitated with an excess of ammonia. After standing several hours the supernatant solution was poured off and the precipitate washed repeatedly by the aid of the centrifuge until a part of the gel was peptized. The remainder was shaken with 75 to 100 cc. of water giving a fairly stable sol which was found to have a pH value of 6.95. A measured amount of this suspension was treated with sodium alizarate solution, a bright red lake resulting. Analysis of the supernatant solution for sodium confirmed the previous observation[1] that most of the element remained in solution as sodium chloride. The results of two such experiments are given in Table III. In these cases the chloride originally present in the alumina as ammonium chloride was displaced by the more strongly adsorbed alizarate ion, while the sodium and ammonium did not exchange. As has been shown,[2] if the chloride ion were first displaced by the strongly adsorbed hydroxyl ion, then little or no alizarate ion will be taken up.

TABLE III

Sol cc	Substancess mixed M/100 sodium alizarate cc	Na_2SO_4 in 75 cc	Na_2SO_4 observed	Na_2SO_4 calculated
100	35	0.0284	0.0506	0.0497
		Na_2SO_4 in 50 cc		
75	25	0.0173	0.0346	0.0355

Alumina gel (from $AlCl_3$) and alizarin. The hydrous alumina gel prepared as described in the preceding section was shaken with water to make 50 cc and mixed with 50 cc of alcohol. On adding 10 cc of a saturated solution of alizarin in alcohol, a bright red lake was formed. In the absence of electrolyte a part of the thoroughly washed gel remained peptized and was not thrown down by prolonged centrifuging. A sample of the supernatant liquid was treated with a drop of ammonia which agglomerated the colloidal lake. The filtrate gave a distinct test for chloride. This was doubtless present as ammonium chloride for the filtrate from a second sample of the red sol, coagulated by a small amount of sodium sulfate, reacted neutral to litmus.

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[1] Weiser and Porter: J. Phys. Chem., **31**, 1829 (1927).

[2] Weiser and Porter: J. Phys. Chem., **31**, 1830 (1927).

The pH value determined with the hydrogen electrode was 6.85. These observations indicate that the alizarin has been adsorbed in exchange with ammonium chloride.

People who regard the red lake as a definite aluminum alizarate would probably consider the formation of a lake under the above conditions as the result of interaction between alumina and alizarin acid. Since the alumina is highly insoluble both in water and in aqueous alcohol and the acid is insoluble in water and very weak such an interaction is a remote possibility. Moreover, as we have seen, a red lake is formed with a sol of aged oxide which is not attacked by very low concentrations of even a strong acid like hydrochloric. Finally, a metathetical reaction between alumina and sodium alizarate or alizarin would not account for the equivalence between the amount of alizarate taken up and chloride thrown out. Certainly, the addition of ammonium chloride to a solution of alizarin or its sodium salt has no appreciable effect on the color.

An alcoholic solution of *aluminum chloride* gives a red solution with alizarin. Since aluminum chloride undergoes marked hydrolysis in water and alcoholysis in alcohol, liberating hydrochloric acid, it is probable that the red alcoholic solution is not a definite aluminum alizarate but alumina with adsorbed alizarate. Aluminum chloride does not undergo reactions analogous to hydrolysis in ether and carbon bisulfide. Accordingly, when alizarin and aluminum chloride are brought together in these solvents the color of the solution is the yellow or orange of the pure alizarin solution.

III. OBSERVATIONS WITH FERRIC OXIDE

Ferric oxide sol and sodium alizarate. Since Sorum has prepared a sol of hydrous ferric oxide free from chloride,[1] it was of interest to determine to what extent this preparation would adsorb alizarate ion. A 50 cc sample of such a sol containing 4 grams of Fe_2O_3 per liter required but 0.45 cc of M/100 sodium alizarate for coagulation. Further addition of dye solution caused peptization of the oxide as a negative sol.

Since dilute ferric chloride is completely hydrolyzed at high temperatures, a dilute sol was formed by adding quite dilute ferric chloride dropwise to boiling water and dialyzing at the boiling temperature short of removal of all the chloride. Such a procedure would be expected to yield a sol entirely free from ferric ion and stabilized by preferential adsorption of hydrogen ion. Actually, a sol containing 0.125 gram per liter gave no test for ferric ion with potassium ferrocyanide even after long standing. A 250 cc portion of this sol was coagulated with 8 cc of sodium alizarate solution. 250 cc of the supernatant solution was evaporated and the residue of sodium chloride converted to sodium sulfate and weighed. The weight was 0.0118 gram, the theoretical amount in the 250 cc being 0.0111 gram. Since the values are approximately equivalent it is evident that chloride ion was displaced by the alizarate while the stabilizing hydrogen ion was not displaced by sodium.

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[1] Such sols doubtless contain a trace of some anion such as nitrate, sulfate, or carbonate.

Conclusions

The formation of hydrous-oxide alizarin lakes is usually an exchange adsorption process in which the relatively strongly adsorbed dye anion displaces a more weakly adsorbed anion such as chloride form the hydrous oxide. If the adsorption capacity of the gel is satisfied with a strongly adsorbed anion such as hydroxyl, little exchange adsorption can take place and lake formation is prevented. Since a bath must be slightly basic in order for alizarin to remain in solution, the necessary adsorption of alizarate ion for suitable lake formation from such baths, takes place only in the presence of a relatively strongly adsorbed cation such as calcium. The mechanism of this process has received extended theoretical and experimental consideration in an earlier paper.[1]

Lakes are formed by the addition of sodium alizarate to positive hydrous oxide sols stabilized by preferential adsorption of hydrogen ion. If the accompanying anion is chloride, the amount of alizarate ion taken up by the coagulated oxide is equivalent to the amount of sodium chloride in the supernatant solution. The addition of an amount of sodium alizarate above the coagulation concentration merely reverses the charge on the sol. Alizarin likewise is adsorbed by the colloidal particles giving a lake which remains in the sol state.

If the oxide gel is formed rapidly in the absence of an anion such as chloride, highly unsaturated atoms of aluminum on the surface will adsorb alizarate from aqueous sodium alizarate solutions or from alcoholic solutions of alizarin acid yielding red lakes. On standing, the highly unsaturated atoms on the surface of the newly formed oxide become oriented into the normal lattice of crystalline alumina and the adsorption of alizarate decreases to such an extent that only a pale pink lake results. The rate and amount of this ageing is appreciably diminished by the adsorption of a chloride, say, since a part at least of the abnormal unsaturation of surface atoms in the rapidly formed oxide is satisfied by the adsorption. An ion more strongly adsorbed than chloride would have a greater retarding action on the rate at which the atoms assume their position in the normal oxide lattice. But as we have seen the presence of an ion more strongly adsorbed than chloride, will correspondingly decrease the adsorption of alizarate by exchange.

In the light of these observations it follows that, depending on the conditions, adsorption of alizarate may be either an exchange adsorption, direct adsorption, or both.

The red color of alumina-alizarin lakes is neither the dark purple to purplish black of the alkali and alkaline earth alizarates nor the orange of the alizarin acid but is a bright red suggestive of the color of the alizarate ion in aqueous solution. The color of the lake is doubtless due to adsorption of the alizarate ion oriented toward the aluminum atom of the oxide. The ion associated with the alizarate ion and oriented toward the oxygen atom

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[1] J. Phys. Chem., 31, 1824 (1927).

of the oxide may be sodium, potassium, ammonium, hydrogen, or calcium without materially modifying the color of the lake except in so far as the extent of its adsorption influences the amount of adsorption of alizarate ion.

In accord with Bancroft's view, the sodium and alizarate ions under certain conditions may be adsorbed in equivalent amounts from sodium alizarate solution. This will be true only in case the oxide is free from adsorbed ions or in case the sodium and alizarate ions displace equivalent amounts of the corresponding ions adsorbed on the oxide during preparation. In any event, the sodium associated with the alizarate is without specific influence on the color of the lake since a similar color is obtained with alizarin acid.

The concept that the alumina-alizarin lake consists of alizarate adsorbed on aluminum atoms might be interpreted to mean that the color is due to a definite aluminum alizarate. Such an interpretation would imply that alizarate radicals are bound to aluminum atoms on the surface of the oxide by primary valence forces; in other words, that two aluminum atoms on the surface hold exactly three alizarate radicals. Followed to its logical conclusion this would mean that sodium, ammonium, or hydrogen alizarate adsorbed by aluminum oxide consists of aluminum alizarate plus sodium oxide, ammonium oxide, or water as the case may be. There is no experimental evidence to justify this conclusion and it is probably incorrect.

Finally, the results of this investigation indicate that the adsorbing power of a substance will be greater and will persist for a longer time if the substance is formed in the presence of ions which are adsorbed during formation and subsequently enter into exchange adsorption with more strongly adsorbed ions.

Summary

The results of this investigation may be summarized briefly as follows:

1. The formation of hydrous oxide-alizarin lakes is usually an exchange adsorption process in which the relatively strongly adsorbed alizarate ion displaces an equivalent amount of a less strongly adsorbed anion from the hydrous oxide.

2. Lakes are formed by adding sodium alizarate to hydrous oxide sols stabilized by preferential adsorption of hydrogen ion. If the accompanying anion is chloride, sodium chloride is found in the supernatant solution in amount equivalent to the alizarate adsorbed.

3. The color of the alumina-alizarin lake is neither the dark purple to purplish black color of thin films of alkali and alkaline earth alizarates nor the yellow orange of the alizarin acid, but is a bright red suggestive of the color of alizarate ion in aqueous solution.

4. The color of the alumina-alizarin lake is due to adsorption of alizarate radicals on the aluminum atoms of the oxide. The ion associated with alizarate may be sodium, ammonium, potassium, hydrogen, or calcium without materially modifying the color of the lake except in so far as the extent of its adsorption influences the amount of adsorption of alizarate ion.

5. A newly formed oxide free from adsorbed ions will form a red lake either from an aqueous solution of sodium alizarate or from an alcoholic solution of alizarin. Lake formation with a pure oxide may be overlooked since such an oxide "ages" more rapidly than one containing adsorbed ions.

6. A pure aged oxide will adsorb but little alizarate ion from an alizarate solution unless the size of the primary particles is such that peptization of the resulting lake as a negative sol can result.

7. Depending on the conditions of formation and the age of the oxide, the adsorption of alizarate may be an exchange adsorption, direct adsorption, or both.

8. A rapidly formed hydrous oxide gel will contain highly unsaturated atoms on the surface. On standing, the unsaturated atoms on the surface gradually orient themselves into the normal crystal lattice of the oxide and the adsorption decreases proportionately. The rate and amount of this ageing is appreciably diminished by the presence of adsorbed ions which may subsequently enter into exchange adsorption with other more strongly adsorbed ions. The significance of this behavior will be discussed in a subsequent communication.

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13-210

THE RÔLE OF THE MEMBRANES IN ELECTRODIALYSIS*

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The fact that small amounts of ionogenic impurities have an important influence upon colloidal behavior has lead to much research on methods of purifying colloidal solutions. Ordinary dialysis is slow and not very thorough. A degree of purification requiring months by this method can often be obtained in a few hours by electrodialysis. This advantage of speed is often offset, however, by unfavorable changes in reaction which may alter the properties of the colloid irreversibly.

In electrodialysis the colloid to be purified is placed in the middle compartment of a three compartment cell between two dialysing membranes. A suitable electrode is placed in each of the outside compartments. These compartments are filled with distilled water which is renewed either continuously or periodically in order to remove the products of electrolysis. Hittorf[1], in his epoch-making studies of transport numbers cautions against the use of membranes to separate the different sections of electrolyte because he observed that one ion was usually retarded more by the membrane than the other. Bethe and Toropoff[2] investigated the effect of membranes more thoroughly and observed that when an electric current was passed through dilute solutions of salts in a cell separated into two compartments by a membrane, that differences in reaction as great as three pH units, occurred at the two sides of the membranes. Membranes which were negatively charged were more permeable for cations than for anions with the result that an excess of anions and an acid reaction developed on the cathode side of the membrane and a corresponding alkaline reaction on the other side. Following the lead of Freundlich and Loeb[3], most investigators of the reaction changes occurring during electrodialysis have assumed that similar differences in the reaction occurred at each side of each of the membranes. Freundlich recommends therefore the use of a negative membrane next to the cathode and a positive membrane next to the anode. The numerous recent investigations of the permeability of membranes by Michaelis and his students[4] furnish further justification for this belief.

Parchment and collodion are both negatively charged and are both satisfactory for use as cathode membranes. No strictly positive membranes are known. Membranes which are positive when used next to the anode in the two membrane electrodialysis system however may be prepared from

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[1] Hittorf: Z. physik. Chem., 39, 613 (1901).

[2] A. Bethe and Th. Toropoff: Z. physik. Chem., 88, 686 (1914).

[3] H. Freundlich and L. F. Loeb: Biochem. Z., 150, 522 (1924).

[4] L. Michaelis and W. A. Perlzweig: J. Gen. Physiol., 10, 598 (1927).

amphoteric substances like the proteins. The membrane most investigated has been the chrom-gelatine membrane first described by Ruppel and his students,[1] and later used by Stern.[2]

This membrane was made by painting a mixture of gelatine, $(NH_4)_2Cr_2O_7$ and glycerine on a support of either wool or silk cloth. The membrane was then "fixed" by exposure to the sun. While most investigators found this membrane superior for use at the anode to collodion or parchment, it frequently showed a "temperamental" behavior.[3] Ettish and Beck[4] attribute the alkaline reaction frequently obtained when this membrane was used to the incomplete removal of the NH_4 of the $(NH_4)_2Cr_2O_7$ in the preliminary washing.

Pauli[5] and his students reduce the reaction disturbance by removing the bulk of the electrolyte by ordinary dialysis then using electrodialysis with very low current densities to remove the last traces of electrolytes. Reiner[6] claims that an ordinary collodion membrane is satisfactory to use next to the anode in the electrodialysis of serum because of Loeb[7] and Hitchcock's[8] observations that collodion strongly adsorbed different proteins. He maintains that a sufficient amount of protein is adsorbed by the collodion during the electrodialysis process to make it act as a protein membrane. A valve-like action is attributed to a pair of such membranes. According to this conception, as soon as the reaction in the middle chamber becomes more alkaline than the isoelectric point of the protein the membranes are negatively charged and hence more permeable for cations than for anions. This would tend to reduce the pH value of the system to the isoelectric point of the protein. If the pH value of the solution were lower than the isoelectric point, then the membrane would be positively charged, and therefore more permeable to anions with the result that the change in reaction would always be toward the isoelectric point and never away from it. Such a system would of course be ideal. Reiner obtained excellent results with his protein solutions but experiments to be cited later show that they are not due to any valve-like action of the type described above.

The objects of the present investigation were: (1) to determine the relative permeability of different membranes to a series of typical anions present in the form of their sodium salts under controlled conditions; (2) to observe and measure (a) endosmosis, (b) changes in reaction in different parts of the electrodialysis cell, (c) current consumption and such other factors as might contribute to an understanding of the permeability observed; (3) to study the effect of the addition of purified colloids of different types upon the rate of removal of the same electrolytes.

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[1] O. Ruppel: Ber. deutsch pharm. Ges., 30, 314 (1920).

[2] R. Stern: Biochem. Z., 144, 115 (1923).

[3] H. Freundlich and F. Loeb: loc. cit.

[4] G. Ettish and W. Beck: Biochem. Z., 171, 448 (1926).

[5] Mona Spiegel-Adolf: Abderhalden's Handbuch der biol. Methoden, Abt. III Teil B 606 (1927).

[6] L. Reiner: Kolloid-Z., 40, 126 (1926).

[7] J. Loeb: "Proteins and the Theory of Colloidal Behavior" (1922).

[8] D. I. Hitchcock: J. Gen. Physiol., 8, 61 (1925).

Experimental Part

The cell used was a modification of the type used by Pauli[1] and was made of Pyrex.[2] The membranes were six centimeters apart and has an effective surface of twenty-five square centimeters each. The electrodes were made of perforated platinum and were slightly smaller than the membranes. They were two or three millimeters from the membrane. In most of the experiments reported, one hundred cubic centimeters of the electrolyte solution to be studied was placed in the middle cell and one hundred cubic centimeters of distilled water in each of the outside cells. From one hundred ten to one hundred twenty volts were applied. A fixed resistance of eighty ohms was kept in series with the cell. The current was read periodically with an ammeter and the total current consumed determined by means of an iodine coulometer. At the end of each run the liquid in each chamber was removed, the volume measured, and the acid in the anode chamber and the base in the cathode chamber and the acid or base in the middle chamber determined by titration. The current was passed usually for twenty or thirty minutes. The diffusion of cations into the anode chamber and of anions into the cathode chamber was found to be negligible in these experiments.

Hemoglobin was selected for the preliminary experiments on the effect of a protein coating on the permeability of collodion for anions. It possesses a combination of properties which make it very suitable for such experiments. (1) Its isoelectric point is very close to the neutral point. If the hypothesis of Reiner concerning the valve-like action of such membranes is valid, the use of this membrane should enable us to avoid harmful extremes of either acidity or alkalinity. (2) Its red color enables us to judge by mere inspection the relative amount of protein absorbed by the membranes. (3) It is readily and irreversibly absorbed by properly prepared collodion membranes. A one to two percent aqueous solution of Merck's hemoglobin was used in all of the experiments reported.

The most difficult point in the preparation of these membranes is to secure just the proper amount of drying of the collodion. The following procedure was found satisfactory for the Schering collodion used. Collodion was poured slowly into the middle of a flat-bottomed Petri dish until the bottom was just covered. It was allowed to dry in the open air for from thirty to forty minutes, then covered with distilled water. After standing in water for from thirty to sixty minutes the membrane was removed from the dish, care being taken not to touch it with the fingers as the trace of grease left prevents the absorption of hemoglobin. The membrane should have a somewhat opalescent appearance when examined by reflected light. If it is dry enough to crackle it will not absorb an appreciable amount of hemoglobin. The collodion membrane is allowed to soak for from twenty to forty hours in a one to two percent solution of hemoglobin which is practically free from salts and not far from the isoelectric point. At the end of that

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[1] M. Pauli: see Mona Spiegel-Adolf, *loc. cit.*

[2] This cell can be supplied by the A. H. Thomas Co., Philadelphia, Pa.

period it assumes a uniform dark red color. The excess protein is washed off and the membrane is ready for use. Such membranes are very stable when used at the anode. Some have been used daily for a month with a great variety of electrolytes without showing any appreciable change.

Table I shows the amount of 0.1N acid transferred to the anode chamber in twenty minutes when using parchment as the cathode membrane and parchment, collodion, and hemoglobin-collodion as the anode membrane.

TABLE I

Influence of the nature of the anode membrane upon the rate of removal of the anions of some sodium salts. Cathode membrane: Parchment.

Electrolyte (100 cc .025N)	cc .1 N acid transferred to anode chamber			Acid-Base ratio		
	Parchment	Collodion	Hemoglobin	Parchment	Collodion	Hemoglobin
NaCl	8.2	13.7	19.4	0.45	0.62	0.99
Na_2SO_4	4.1	11.8	19.0	0.27	0.60	0.93
NaH_2PO_4	1.8	1.9	18.5	0.11	0.13	1.13
Na_2HPO_4	1.0	4.9	9.9	0.17	0.35	1.66
Na-Acetate	0.8	1.7	10.3	0.24	0.30	1.60

TABLE II

Influence of the nature of the anode membrane on resistance and electrodialytic efficiency. Cathode membrane: Parchment.

Electrolyte (100 cc .025 N Soln.)	cc .1 N Iodine liberated in Coulometer			Electrodialytic Efficiency		
	Parchment	Collodion	Hemoglobin	Parchment	Collodion	Hemoglobin
NaCl	64.7	77.6	54.5	0.41	0.46	0.71
Na_2SO_4	41.1	61.0	46.3	0.47	0.52	0.85
NaH_2PO_4	17.3	37.2	35.3	0.52	0.45	0.98
Na_2HPO_4	12.4	31.4	11.6	0.56	0.60	1.37
Na-Acetate	6.8	11.6	12.4	0.62	0.62	1.32

Collodion is much more permeable for anions than parchment and the hemoglobin coating increases its efficiency still further. The ratio of acid to base removed is as near one as could be expected in the case of the salts of the strong acids, but more acid than base is removed in the case of the weak acids which results in a decidedly alkaline reaction in the middle chamber. The data presented in Table II taken from the same experiments show that less current was used in the experiments with the hemoglobin membrane. If the amount of acid found in the anode chamber is added to the amount of base found in the cathode chamber and the sum divided by the amount of iodine liberated in the coulometer which was in series with the cell the value

E which has been termed "the electrodialytic efficiency" is obtained. This value is very much higher for the hemoglobin membrane than the others. For the strong electrolytes it is always less than one but for the salts of the weak acids it is appreciably above one.

The volume changes which occurred, and the excess of acid or base found in the middle chamber are shown in Table III. Parchment shows little or no endosmosis. Collodion endosmoses as if negatively charged while the hemoglobin-collodion is positively charged in every case, although the reaction of the liquid in the middle chamber is strongly alkaline in the case of the salts of the weak acids and slightly acid in the case of the salts of the strong acids. The maximum endosmosis which we usually associate with a maximum charge is obtained with Na acetate, with which the most alkaline reaction in the middle chamber was also observed. This membrane has a strongly positive charge in spite of the fact that the pH value of the liquid in the middle cell is much more alkaline than the isoelectric point of hemoglobin. The data shown in Table IV are still more convincing evidence that the valve-like action theory of the behavior of protein-coated collodion membranes advanced by Reiner is not in harmony with experimental facts. In this series of experiments, the same two membranes, one of parchment, the other of hemoglobin-collodion were used at both cathode and anode for the electrodialysis of a series of salts. The endosmosis data shows that the hemoglobin-coated membrane was positively charged when used at the anode in spite of the alkalinity which developed in the case of the Na acetate and Na_2HPO_4 solutions and that it was negatively charged when used at the cathode even when the pH value of the solution in the middle chamber fell lower than 2.5. If the charge on the membrane is independent of the reaction of the liquid in the middle chamber within such wide limits what are the essential conditions for controlling the charge on the membrane? The above experiments show that the hemoglobin membrane was in every case positive when used at the anode and negative when used at the cathode. This would indicate that the charge on the membrane is determined *by the reaction in the*

TABLE III

Volume and reaction change in the middle chamber. Cathode membrane—parchment.

	Anode Membrane Parchment		Anode Membrane Collodion		Anode Membrane Hemoglobin	
Electrolyte (100 cc .025 N. Solution)	Volume change in cc	Excess acid cc .1 N	Volume change	Excess acid cc .1 N	Volume change	Excess acid or base cc .1N
NaCl	0.0	11.8	3.0	7.2	−10.0	.35 acid
Na_2SO_4	0.0	12.5	3.0	8.9	− 6.0	1.80 "
NaH_2PO_4	0.0	8.6	5.0	12.7	−17.0	1.60 base
Na_2HPO_4	0.0	6.7	3.0	9.3	− 8.0	2.33 "
Na-Acetate	0.0	3.8	4.0	3.5	−22.0	2.60 "

membrane. This was clearly demonstrated by the use of serum albumin-coated collodion membranes which were soaked in a solution of methyl red. The methyl red was strongly absorbed. When placed in the electrodialysis cell the membrane next to the cathode became yellow almost immediately while that next to the anode became red. These colors observed in the membrane were independent within rather wide limits of the reaction of the liquid in the middle chamber. The reaction changes within the middle chamber were studied further by filling it with a hot two percent agar solution containing a salt solution and methyl red and phenolphthalein. This solution was allowed to gel. A few seconds after the current was applied the red acid color of methyl red developed inside the anode membrane and a similar red due to phenolphthalein developed inside the cathode membrane. These two red zones gradually approached each other as the electrodialysis proceeded. In this experiment the products of electrodialysis were continuously removed by a rapid stream of distilled water. This experiment indicated that a hydrolysis takes place at and under certain conditions even in the middle chamber as a result of the separation of the two ions by means of the applied potential. The situation may be considered analogous to the so-called membrane hydrolysis, with the difference that, in the present case, the diffusion of the one ion is prevented by the applied potential instead of by its inability to pass through the pores of the membrane on account of its

TABLE IV

Effect of reversal of polarity on rate of electrodialysis of a series of salts between a parchment and a hemoglobin-collodion membranes. Volts 110, time 20 minutes. H—hemoglobin membrane next to anode. P—parchment.

Electrolyte (100 cc .025 N)	Acid Removed cc .1 N		Base Removed cc .1 N		Acid-Base Ratio	
	H	P	H	P	H	P
NaCl	19.35	4.35	19.60	11.5	.99	.38
Na_2SO_4	19.2	2.65	20.5	11.20	.94	.24
NaH_2PO_4	18.5	1.10	16.3	9.15	1.13	.12
Na_2HPO_4	9.9	.85	5.9	5.20	1.68	.16
Na-Acetate	10.3	.60	6.2	2.7	1.66	.22

Electrolyte (100 cc .025 N)	Current (cc .1 N iodine liberated)		Endosmosis *in cc to* Anode Cathode	
	H	P	H	P
NaCl	54.5	28.4	11.	10.
Na_2SO_4	50.35	24.6	8.	10.
NaH_2PO_4	35.3	19.1	17.	6.
Na_2HPO_4	11.6	12.75	9.	4.
Na-Acetate	12.95	6.8	20.	2.5

size. As further evidence of such hydrolysis in the middle chamber may be cited experiments in which salts which yield insoluble hydroxides on hydrolysis such as $MgSO_4$ and $AgNO_3$ were electrodialysed. As soon as the current was applied, a copious precipitation of the hydroxides of these metals occurred inside the middle chamber at the cathode membrane. Salts of slightly soluble acids like the soaps and Na salicylate likewise yielded a precipitate of acid inside the middle chamber at the anode membrane. The behavior of the protein-coated membranes described above is readily understood in the light of these experiments.

The hemoglobin membranes considered thus far were coated on both sides with the protein and were symmetrical when used for electrodialysis. The permeability of membranes coated on only one side with protein was found to vary with the position of the coating. The data given in Table V show that the membrane is more permeable for anions when the protein coating is on the inside (next to the solution being dialysed). The resistance of the membrane is from two to four times as great in one direction as in the other. This behavior seems somewhat analogous to that observed in certain physiological membranes.

TABLE V

Effect of reversing a collodion membrane, with a hemoglobin coating on one side only, upon its efficiency when used as an anode membrane. 110 volts, 20 minutes. Cathode membrane — Parchment.

Electrolyte (100 cc .025n)	cc .1 N Acid removed		cc .1 N Base removed		cc .1 N Iodine liberated	
	Hb. inside	Hb. outside	Hb. inside	Hb. outside	Hb. inside	Hb. outside
NaCl	16.0	8.85	21.7	13.1	67.7	29.4
Na_2SO_4	13.9	6.0	20.4	10.6	56.4	22.5
NaH_2PO_4	8.9	2.8	17.8	6.6	39.6	12.4
Na_2HPO_4	14.9	3.21	16.0	4.65	34.0	9.1
Na-Acetate	5.4	1.21	6.9	2.9	14.7	6.0

In all of the experiments cited above, only dialysable salts were present. The question now arises as to the effect of the presence of different types of colloidal material upon the rate of removal of these same salts through these same membranes under the same experimental conditions. In the experiments cited in Table VI fifty cubic centimeters of a previously electrodialyzed colloidal clay, bearing a negative charge, was added to the middle compartment of the cell in addition to the electrolyte. The rate of removal of the anions is in every case retarded. Salts from which the anion was removed more rapidly than the cation in the absence of the clay now show the reverse behavior. This effect seems analogous to that observed above in the case of the unsymmetrical protein membranes. The addition of the negative clay causes the formation of a negative layer on the inside of the anode membrane. This coating tends to counteract that of the positive hemoglobin coating.

Carefully purified gelatine was used in a similar series of experiments. It did not have any retarding influence, in fact in a few cases the removal of the ions of the salt seemed to be accelerated in the presence of the gelatine. Positive sols would be expected to deposit on the cathode membrane and to retard the removal of the cations. Experimental verification of this is still lacking.

The hemoglobin membrane seems well suited for use with the salts of strong acids but leads to the development of an alkaline reaction in the case of the salts of the weak acids. Would the use of a protein with a more acid isoelectric point be better suited for use with such systems? Experiments made with Ettish and Ewig[1] using a membrane coated with protein absorbed from a sample of electrodialysed serum indicate that such is the case. The alkaline reaction obtained with serum and Ringer's solution when the hemoglobin membrane was used was avoided by the use of a membrane prepared from electrodialyzed serum with a pH value of 5.4. All electrolytes studied with this membrane gave a lower acid-base ratio than when the hemoglobin membrane was used. It is quite evident, in the light of all of the experiments described above, that there is no single electrodialysis system that is completely satisfactory for all types of purification. The effect of the colloid being purified and the nature of the electrolyte to be removed must both be taken into consideration.

TABLE VI

Effect of a purified colloidal clay upon the rate of removal of added salts expressed as percent of total removed in one hour, 110 volts. Membranes: Anode-Hemoglobin, Cathode-Parchment.

Electrolyte (100 cc .025 n)	No Clay		Clay present	
	% Anion removed	% Cation removed	% Anion removed	% Cation removed
KCl	98.0	98.0	92.0	96.0
Na-Acetate	54.0	43.0	18.5	22.0
Na_2HPO_4	42.0	34.5	13.5	19.0

Summary

1. Membranes prepared by soaking properly prepared collodion membranes in certain protein solutions are much more permeable to anions than the untreated collodion or parchment commonly used in electrodialysis.

2. These protein-covered membranes do not possess, however, a valve-like action, i.e., ability to change sign of charge when the pH value of the liquid being purified passes through the isoelectric point of the protein used;

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[1] G. Ettish, R. Bradfield, and W. Ewig: Kolloid-Z., 45, 141 (1928).

but are positively charged when used next to the anode and negatively charged when used next to the cathode except in extremely low or extremely high pH values.

3. Membranes coated with proteins having a relatively high isoelectric point where found to be more permeable to anions than those having a low isoelectric point.

4. The nature of the salts to be removed determines the choice of the protein. For salts of strong acids and bases the hemoglobin membrane is very satisfactory. For salts of weak acids, proteins with lower isoelectric points such as serum or egg albumin give less disturbance of the reaction of the solution being purified.

5. The course of the electrodialysis is complicated further by the action of the colloid being purified. Negative sols tend to deposit on the anode membrane and to retard thereby the passage of the anions through the membrane. Amphoteric sols, as a rule, show no retarding influence. Positive sols would be expected to retard the removal of cations but they have not yet been studied in detail.

Acknowledgment

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216543

THE PLASTICITY OF CLAY

BY LEON E. JENKS

Object of Investigation

Plasticity of clay has been ascribed to lamination, to the presence of colloids, to the presence of organic matter, and to the presence of inorganic salts. Bancroft[1] says: "If we have a gelatinous film which is adsorbed strongly by the solid particles and which can take up and lose water, we shall have plasticity. In the case of clay the gelatinous material may be hydrous alumina, hydrous silica, or some intermediate composition. The difficulty, however, is to account for its remaining plastic after moderate drying and for its readsorbing water to form a gelatinous mass. This is probably due to the presence of some salt, but we do not know what salt and consequently we cannot tell why one clay is plastic and another not, and we do not know what to add to a non-plastic clay to make it plastic." The object of this investigation is to find out if any salt would allow such gelatinous materials to become gelatinous again after moderate drying and remoistening with water.[2]

Dumont[3] seems to have been the first to suggest that "the active colloidal material is a jelly-like or amorphous mass enveloping the solid grains of material." This idea was extended by A. D. Hall's[4] suggestion that "as there can be no definite outer surface of the colloidal envelope, it may be considered as surrounding the soil particles in a series of shells of gradually increasing hydration so that there is a continuous transition from a solid nucleus to a solution." E. Podszus[5] considers that "the coagulation of substances in the sol form is the essential feature of plastic systems." Mellor[6] credits A. Baumé as the first to connect plasticity of clay with the presence of saline matter. Purdy[7] has advocated this consistently, and Purdy and Moore[8] give as "an extremely probable assumption that it is the influence of adsorbed salts that gives clay its plasticity."

The term clay is used in this paper to describe the materials known to the ceramist as clay. The special clays were furnished very courteously by the Research Laboratory of the Norton Company of Worcester, Mass. The object of this paper is to determine what salt or salts will keep an alumina-rich or a silica-rich gelatinous film on a clay grain in such a state

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[1] "Applied Colloid Chemistry," 160 (1921).

[2] This is excluding the action of humus, which tends to make clay plastic.

[3] Dumont: Compt. rend., 149, 1087 (1909).

[4] "The Soil," 34 (1912).

[5] Kolloid-Z., 29, 65 (1917).

[6] Trans. Faraday Soc., 17, 354 (1922).

[7] Trans. Am. Ceramic Soc., 11, 590 (1911).

[8] Trans. Am. Ceramic Soc., 9, 222 (1907).

that it will take up water again and become gelatinous after having been dried moderately. In Table I are given the chemical analyses of the clays as furnished by the Research Laboratory of the Norton Company. The Florida washed kaolin, the Bramlett, and the Kentucky No. 5 are the ones referred to most frequently in this paper.

TABLE I

Chemical Analyses of the Clays used

	Albany Slip	Allen*	Bramlett	Shippach	Kentucky No. 5	Florida Kaolin washed**
Al_2O_3	12.17	25.08	24.69	24.37	27.66	39.19
Fe_2O_3	1.63	2.22	2.24	2.08	0.88	0.45
FeO	3.29					
SiO_2	60.21	55.35	57.86	51.22	57.34	45.39
TiO_2	0.70	0.40	1.30	1.25	2.20	
CaO	6.55	0.22	0.45	trace	0.35	0.51
MgO	3.04	0.65	0.32	0.00	0.18	
Na_2O	1.60	0.72	0.41	1.51	0.59	0.83
K_2O	2.62	2.48	0.57	1.68	0.85	
H_2O	0.49	2.30	2.83	7.80	1.07	14.01
Loss	8.05	11.26	8.84	10.18	9.71	

* The Allen is a bond clay from Maryland which approaches more nearly the characteristics and properties of the German Klingenberg clay than any other American clay yet discovered. It is high in carbonaceous matter occurring as charcoal and contains traces of gypsum.

The Bramlett is a bond clay from Mississippi.

The Shippach is a German clay. Communication from the Norton Laboratories.

** Ries: "Clays and Their Industrial Use," 407 (1927).

Experimental

The Bonding Power of Gelatinous Alumina-Silica Mixtures containing Electrolytes.

To determine what salts keep the films on clays gelatinous and to see whether these films are alumina-rich or silica-rich, experiments were made on gelatinous alumina, gelatinous silica, and mixtures containing approximately 75-25, 50-50, 25-75 molecular percents of alumina and silica. The salts chosen were sodium chloride, carbonate, hydroxide, phosphate, and sulphate, salts likely to be present in natural waters. Two amounts of each salt were taken, which are called maximum and minimum. The amounts for sodium hydroxide were 0.5 g and 0.02 g per gram of the dried material, correspondingly approximately to 37% and 1.5% Na_2O.

Preparation of Materials

Gelatinous Silica.

A slight excess of C.P. hydrochloric acid was added to a commercial water-glass solution. The gelatinous mass was suspended in a muslin bag and dialyzed against distilled water until the water gave no test for chloride with silver nitrate. This does not prove the absence of chloride in the silica.

Gelatinous Alumina.

A slight excess of a sodium hydroxide solution was added to solutions of aluminum chloride and aluminum sulphate. The precipitates were dialyzed until no test for chloride was obtained with silver nitrate and none for sulphate with barium chloride. As before, this does not prove the absence of chloride or sulphate in the alumina.

Mixtures of Gelatinous Alumina and Silica.

Solutions were made up of water-glass with or without caustic soda, and of aluminum sulphate, chloride, or acetate with or without hydrochloric acid, such that on mixing the precipitate had approximately the right ratio of alumina to silica and the solutions were slightly acid. The precipitates were purified as far as possible by dialysis.

The gelatinous materials, alumina, silica, and the three mixtures of different molecular proportions, were dried on a water-bath, remoistened with water and molded by hand into balls. On standing exposed to the air all night, all crumbled to powder or did so when a slight pressure was obliged. The effect of adding electrolytes is shown in Table II.

TABLE II

Bonding Strength of Water-Bath-Dried Material after remoistening and Air-Drying

Material	Electrolyte added								
	None	NaCl		Na_2CO_3		Na_2HPO_4		NaOH	
		Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Al_2O_3	o	o	e	e	o	o	o	o	2
$3Al_2O_3.SiO_2$	e	o	o	e	e	e	e	e	e
$Al_2O_3.SiO_2$	p	p	p	p	e	p	p	p	2
$Al_2O_3.3SiO_2$	p	p	p	p	e	p	p	p	2
SiO_2	p	p	p	p	p	p	p	p	1

p—Powdered on drying in the air or easily crushed.
e—Not powdered by drying the air or on a water bath.
Readily crumbled with slight pressure.
After heating in steam bath very easily powdered between the fingers.
o—Not powdered by drying in the air or on a water bath, but not too hard to crush between the fingers.
Too hard to crush between the fingers after heating in a steam bath.
1—A glass-like mass.
2—Sticky mass that did not dry on standing 24 hours.

Additional experiments were made with the 75-25 alumina-silica mixture, using a gelatinous alumina prepared from aluminum acetate. The data are given in Table III.

A Method for the Measurement of Relative Plasticity of Clay.

The results tabulated in Table III are not only unsatisfactory in themselves, but they depend too much on the personal judgment of the experimenter. The conclusion was reached that no real progress could be reached until some method was adopted that would allow the bonding power of the gelatinous film or mass to be evaluated numerically. At the time this experimental work was being done (1921), the absence of a standard method, or even of a universally accepted method for measuring the plasticity of clay, made an arbitrary choice necessary.

Preliminary experiments showed that a ball of clay moistened to plasticity breaks down into smaller particles when placed in an excess of water; that the air-dried ball of clay that had been moistened to plasticity behaves similarly; that the time for the disintegration of a ball of air-dried clay depends upon the kind of clay taken; and that the same time was required for the disintegration of the ball of clay when the mud from a disintegrated ball is dried, moistened to plasticity, and tested again. It was found that a clay moistened to its best plasticity, as shown under the thumb, gives the highest relative plasticity value for that material. It was also found possible to arrange several commercial clays in the same order of relative plasticity as they are arranged by the ceramic engineer. In this paper the time of disintegration of a clay ball will be taken as a measure of the relative plasticity of that clay at that temperature. The test as adopted is described in the next paragraph.

TABLE III

Effect of Alternate Drying and Remoistening on Bonding of $3Al_2O_3.1SiO_2$ Mixtures.

Times dried	Electrolyte added										
	None	NaCl		Na_2CO_3		Na_2HPO_4		NaOH		Na_2SO_4	
		Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
2	p	e	o	e	e	p	p	p	e	e	1
3	e	e	e	p	o	p	e	p	o	p	1
4	e	e	e	e	o	e	e	e	o	p	o

p—Powdered on drying in the air.
e—Not completely powdered on drying in the air but very soft.
o—Remained hard after drying in the air.
1—Plastic after drying for 16 hours in the air.

Plasticity Test

Five grams of clay, dried and ground as for commercial use, was weighed out, moistened with water to optimum plasticity—as determined under the thumb—well kneaded and molded into a ball in the palm of the hand, allowed to dry for one day in the air, and the air-dried ball so placed in an excess of water at room temperature that as the ball of clay disintegrated, the sedimented particles would fall away from it. The time in minutes taken for the disintegration of the ball of clay to a mud gives the measurement of the relative plasticity of the clay.[1]

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[1] Talwalkar and Parmelee named this test the "Bancroft Test" (J. Am. Ceramic. Soc., 10, 673 (1927)). If it proves to be an acceptable and a satisfactory test, I would choose that it be known by this name. It is a modification of the Sokolow method.

In Table IV are given the plastic values, as determined by this method, of the ceramic materials obtained from the Norton Company. No value is given for the Bentonite clay. The clay swells up and does not flake off as do the other clays. The effect of this swelling as a disturbing factor has not been worked out.

TABLE IV

Plasticity of some Commercial Clays and Ceramic Materials

Clay	Plasticity	Clay	Plasticity
Albany Slip (New York)	4	Highland Pot	10
Allen (Maryland Bond)	30	Kaolin (Florida Washed)	4.5
Bentonite		No. 5 Kentucky Bond	15
Norton Bond B	8	No. 6 Kentucky Bond	12
Bramlett (Mississippi Bond)	60	Lignite Clay	7
Brimfield (Connecticut Valley)	8	Sandy Open	0.5
Feldspar	2	Shippach (Germany)	25
Fuller's Earth	6		

In Table V are given the data, as found by this test, for the experiments recorded in Table III.

TABLE V

Effect of Alternate Drying and Remoistening on the Plasticity of the $3Al_2O_3.1SiO_2$ Mixtures

Electrolyte added	Plasticity after times dried		
	Two	Three	Four*
		1	1
Min. NaCl	10	4	1
Max. NaCl	10	15	1
Min. Na_2CO_4	8	1	1
Max. Na_2CO_3	10	15	1
Min. Na_2HPO_4	4	1	1
Max. Na_2HPO_4	10	2	1
Min. Na_2SO_4	4	1	1
Max. Na_2SO_4	10	15	1

* The values in this column are too high.

The Mechanism of the Plasticity Test.

The real difficulty in using the time of disintegration of a ball of clay as a measure of relative plasticity is in the molding of the test ball. To obtain concordant and, at the same time, correct results, it is necessary that every precaution be taken to mold the test balls with that amount of water that will develop its highest plasticity. If the test ball is molded too wet or too dry, the measure of the relative plasticity obtained will be too low. If the test is run on too dry material, the error may escape attention; if the clay was too wet when it was molded, it would be sticky under the thumb. The necessity for observing every precaution in the molding of the test balls, so that the amount of liquid used will give the maximum amount of relative plasticity, is shown by the time of disintegration of test balls of Bramlett clay molded in ammonia water, which gives a greater difference than is easily obtained with water alone (Table VI) and by the effect of too much water (Table VII) which was obtained by molding the clay when it was very sticky. A clay molded when sticky and allowed to dry in the air spalls under water with larger flakes than when it is molded with the optimum amount of water. These larger flakes slowly break down into a mud that may not be readily tamped into a plastic mass with a glass rod. The total time taken for the sample molded with too much water to become a non-plastic mass was approximately equal to the time of disintegration of the test ball molded at optimum plasticity, but the end-point was very difficult to get.

Table VI

Effect of not molding with Optimum Liquid Content

Clay	Molding fluid	Condition molded	Disintegrating fluid	Time
Bramlett	Ammonia water	Too wet	water	16 min.
"	Ammonia water	Too dry	"	10 min.
"	Ammonia water	Optimum	"	40 min.

Table VII

Effect of molding a Clay with too much Water*

Clay	Plasticity found	True plasticity
No. 5 Kentucky	9	15
Fuller's Earth	4	6
Feldspar	0.5	2
Bramlett	55	60

* One effect of molding a clay with too much water for optimum plasticity is to develop stickiness in the material.

As noted before, when the clay is molded too wet there is a residual plasticity in the spalled flakes. By tamping or stirring the sediment after the disintegration of the test ball, the residual plasticity may be approximately determined but it will not be correct to interpret all residual plasticity as the result of molding with an excess of water. There are some clays that give residual plasticity when molded with optimum water content. In Table IV it is shown that No. 5 Kentucky Bond clay has a lower relative plastic value than the Allen clay. The spalling of the Kentucky clay gives a flaky sediment of a determinable plastic value while the Allen clay gives a non-plastic mud. It would not be correct to interpret the experimental results as showing that the Kentucky clay was not molded at optimum plasticity, or that the plasticity of the Kentucky clay was superior to that of the Allen clay. The correct interpretation would be that, when molded with the optimum water content, the plasticity of the Kentucky clay was not completely developed. The practice of stirring or gently tamping the spalled mud is a good one; not only do you get a better idea of the working properties of the clay but you also get some knowledge of the possibilities of improving the plasticity where a more plastic clay is desired.

The time of drying the test balls of a clay seems to influence the plastic value less than the amount of water used in molding. Table VIII gives the relative plastic values obtained by drying clays for different lengths of time. Where small differences are shown, these may be entirely due to the amount of water used in the molding. All samples were molded under the thumb to maximum plasticity. Large differences may not be so explained, as the plastic values of samples of a clay whose moisture content is but little different, vary on a smooth curve, with a maximum plasticity at the optimum water content. The paper of Mellor[1] which was obtained after this part of the work was done, gives a curve showing the relation between the amount of water and plasticity as obtained by his method of measurement. The two methods agree as to the effect of the amount of water present.

TABLE VIII

The Effect of the Time of Drying on Relative Plasticity

Clay	Time dried in air			
	20 hours	2 days	4 days	12 days
Albany Slip	4	4		
Allen	30	22	28.5	28
Bramlett	60	62	50	60
No. 5 Kentucky	14		14.5	14.5
No. 6 Kentucky	12		10	9.5
Highland Pot	9.5		9.5	10
Shippach	25.5		22	

Mellor's[2] "criterion" is that "no known property of the dried clay can be used as an infallible index of the plasticity of the wet clay, and measurements of plasticity dependent on some property of the dried clay can therefore be dismissed because even though they may measure an important property of clay, that property is not plasticity." To meet Mellor's criterion, most of this work having been done before his paper was obtained, a study was made of the slacking time of clays when they were moistened to maximum plasticity, as shown under the thumb. Samples of commercial clays were molded under the thumb with the optimum amount of distilled water and without drying were placed in an excess of distilled water at different temperatures.

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[1] Trans. Faraday Soc., **17**, 354 (1922).

[2] Trans. Faraday Soc., **17**, 354 (1922).

In Table IX the time of disintegration at 60°C is multiplied by three for the purpose of ready comparison with the values given in Table IV. A choice of different temperatures would make possible a differentiation between materials that were little plastic and also between materials that were highly plastic. At room temperature the time of spalling of a plastic clay was very long and at 80°C it was very short. The temperature of 60°C was chosen as giving a sufficiently sharp differentiation for the clays used. For the valuation of ceramic materials of very low plasticity a much lower temperature would be more satisfactory.

TABLE IX

Disintegration Time of Moist Clays at Different Temperatures

	Time of disintegration at			Time at 60°C times three
	20°C	60°C	80°C	
Albany Slip	100	14		42
Allen	110	2.5		22
Bramlett	100	22		66
Brimfield	100	5		15
Highland Pot	40	3.5		10.5
Kaolin Fla. washed	100	3		9
No. 5 Kentucky	90	5	2	15

The amount of water used in the molding of the test balls, that are disintegrated while they are plastic, is as important as it was when the air-dried balls were used. A sample of No. 5 Kentucky bond clay molded at stickiness gave a slacking time of 3.5 when the plastic clay was placed in water at 60°C. This sensitiveness to the amount of water present, while very annoying, cannot be used as an argument against any method of testing plasticity that does not show with increasing amount of water that plasticity passes through a maximum is, to quote Mellor, "testing some other property than plasticity." As more than the optimum amount of water gives less than the maximum relative plasticity by this test, it does not seem to be a method for the measurement of the stickiness of clay. Also, to quote a ceramic engineer[1] "in the grading of the Bramlett and the Allen clays many would place the Allen first. This difference of opinion arises from the fact that some of us distinguish between plasticity and stickiness. The Allen clay is not as moldable, that is, plastic, as the Bramlett but there is no question but that it has greater stickiness." The methods of testing plasticity developed here show that there is no question of the superiority of the Bramlett clay over the Allen clay.

The only serious change in relative plasticity when the plastic material itself was allowed to spall under water, in place of the air-dried material, was the change in the position of the Shippach clay. This is not accounted for here. That the change in the position of the Albany and the Brimfield clays was due to the carbonates present was shown from the increased time

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[1] Personal communication from M. F. Beecher.

of disintegration for the other clays when a small amount of a carbonate was added and the plastic clay placed under water. The relative plastic value as obtained by the "Dry Method" seemed more correct than that obtained by the "Wet Method." The Allen and the Shippach clays are considered by ceramic engineers to have the same plastic values and both are inferior in moldability to the Bramlett clay. Also, the time of disintegration of the pellet of moist clay gave results that did not seem always to check well with the test under the thumb, nor were they as satisfactory in this respect as the results obtained with the air-dried pellets. However the use in this paper of the results obtained on air-dried materials does not imply a rejection of Mellor's criterion. Unless a clay dried in the air for several days would be included as a wet clay, the application of this criterion here is doubted as a short air-drying did not remove enough water to destroy the film. The time of disintegration of the air-dried material is the method used in the rest of this paper, unless it is definitely stated that the moistened material was tested.

Table X

Relative Plasticity of Clays obtained from Air-dried and from Plastic Materials

From Dried Clay		Clay at Maximum Plasticity	
		Shippach	90
Bramlett	60	Bramlett	66
		Albany	42
Allen	30	Allen	22
No. 5 Kentucky	15	No. 5 Kentucky	15
		Brimfield	15
Highland Pot	10	Highland Pot	11
Brimfield	8		
Kaolin	4·5	Kaolin	9
Albany	4		

Plasticity in Clays from added Electrolytes.

The problem of the effect of adding electrolytes to a gelatinous alumina-silica film was again attacked. No progress was made until kaolin was substituted for the alumina-silica mixtures. A moist clay has a distinctive feel under the thumb that is characteristic. Even a clay having as little plasticity as a washed kaolin has to some degree the "feel" of body, of uniform yield, of smoothness both of resistance and of mobility,—that indefinable something which the thumb recognizes as characteristic of a clay. The alumina-silica mixtures did not have this. When moistened to mobility there was the feel of emptiness and not of body, the yield and the feel that was characteristic of finely ground sand and not of a clay. The added carbonates had given a stickiness when moist and a stone-like mass upon drying. Where air-dried clay will usually rub away easily when abrased and drying in a steam bath give a softer feel, the alumina-rich mixtures gave a harder material the more complete the drying; and when the drying was made very slow through the occasional addition of a drop of water to the surface of a drying pellet, the mass set to a stone. I was convinced that the mixtures when dried had too coarse a structure to be classed as clays. Kaolin was chosen because it had the "feel of a clay." It was known to contain very little material that was not alumino-silicic. It had a little plasticity, something that could be built on, as a true plasticity. With kaolin definitely chosen as the alumina-silica material and the plasticity test as the method of measurement, the decision was made to use the common salts of all the alkali and alkaline earth metals usually reported in an analysis of a clay. Lithium salts were added later because of the known presence of lithium salts in sea water.[1] The following procedure was then adopted to study the effect of added electrolytes on the plasticity of clay. A known weight of a C.P. salt was added to a dilute slip containing 5 grams of the clay. The water was evaporated off on a water bath. The dry residue, moistened to maximum plasticity as determined under the thumb, was molded into a ball, which was air-dried and used for the plasticity test as outlined above. In the recording of the results

TABLE XI

Effect of Alkaline and Alkaline Earth Chlorides on Kaolin
Amount of Kaolin is five grams

No.	% Salt	Plasticity					
		$LiCl$	$NaCl$	KCl	NH_4Cl	$CaCl_2$	$MgCl_2$
1	0.00	4.5	4.5	4.5	4.5	4.5	4.5
2	0.05	6.5					
3	0.10	10	4.5			4.5	
4	0.25	16	6.5			5	
5	0.50	16	6	4.5	3	4.5	4.5
6	1.00	15.5	5.25	4.5	3.25	6.25	6
7	2.00	14.5	5	3	5	7	6.5
8	4.00	14	4	3	3	7	5.5
9	6.00	12	3.5	3	3	6.5	5
10	8.00	14	7.5	3	5.5	8.5	6
11	9.00	12.5	200	3	15		6
12	10.00	26*	200	3	200	8	6
13	11.00			3.25			
14	12.00	25.5*	200	200		180	46
15	14.00		200			180	200
16	16.00	30*	200				200

* These experiments were made on another sample of Kaolin, the plasticity of which did not exceed 4.5.

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[1] Clarke: "Data of Geochemistry," 4th edition, 119.

the weight of salt used is always expressed as a percentage of the weight of clay taken and the time in minutes required for the disintegration of the air-dried test ball in an excess of water is given as plasticity.

When an alkaline or an alkaline earth chloride was added to kaolin, the plasticity of which was 4.5, a noticeable increase in plasticity was observed, both when tested under the thumb and by the plasticity test. The results obtained by the plasticity test are given as Table XI. An increase in plasticity was obtained only after the amount of added chloride was in excess of a definite value, critical concentration specific for each salt. Each chloride at some concentration gave to the kaolin an increased plastic value. When the plastic value obtained was below 70, the plasticity could be compared under the thumb with that of commercial clays. As no commercial clay was available that gave values as high as 100, values above 70 could not be interpreted.

The value 200 expresses that the time required for the spalling of the test ball was very long. No account was taken of actual numerical values after an elapsed time of three hours, as the loaded feel under the thumb of these clays that gave such high spalling seemed entirely different than the plasticity of the Bramlett which was the most plastic of the commercial clays used for the purpose of comparison. The molecular concentration of the chlorides where the plasticity test value first reached an approximate value of 200 is

$LiCl$	$NaCl$	KCl	NH_4Cl	$CaCl_2$	$MgCl_2$
—	0.153	0.16	0.19	0.11	0.12

where the figures are expressed in the percentages of the salt divided by the molecular weight of that salt. These amounts of salts would give the following approximate amounts of saturated solutions at room temperature:

	$NaCl$	KCl	NH_4Cl	$MgCl_2$
Grams of salt used	0.45	0.60	0.50	0.70
Approx. cc of saturated solution	1.25	2	2	1.3

which are within the range of the amounts of water required to moisten the clay for plasticity. With much added salt there is a scum of salt formed on the surface of the air-dried clay, so all the added material did not remain within the pellet. This scum becomes more pronounced the larger the amount of added salt. When no surface scum is present, it is interpreted that the drying surface of the test ball was never wet with a saturated solution of the salt. When there is a surface scum, then there is appreciable loss of water after the formation of a saturated solution at or near the surface. With the addition of potassium chloride the presence of a surface scum could be detected with 8% of the salt but not with 6%. With 11% of potassium chloride there were well-developed crystals formed on the surface of the clay. From these observations the conclusion is formed that the excessively high plasticity values did not depend upon the formation of saturated salt solution. There was no actual change in the plasticity of the kaolin brought about by the use of large percentages of a salt, as the increase in plastic value did not remain when the material was made into a slip and electrolyte decanted off.

With the exception of the salts of lithium, the high plasticity values obtained through the addition of a salt to kaolin would not survive the re-formation of a dilute slip, the decantation of most of the supernatant liquid after the clay had been allowed to settle, the drying to plasticity, and the air-drying of the molded material.

Table XII

Effect of Decantation of Electrolytes on Plasticity
Amount of Kaolin is five grams

No.	Electrolyte added	Plasticity after times decanted		
		None	Once	Twice
1	10% NaCl	200	3	
2	12% KCl	200	2.5	
3	1.5% LiCl	16	18	
4	1.0% LiCl	15.5	18	11
5	0.5% LiCl	16	15	10.5

The molecular concentration of the chlorides where their addition gave the first unmistakable rise in plastic value is

	$LiCl$	$NaCl$	KCl	NH_4Cl	$CaCl_2$	$MgCl_2$
% salt	0.05	0.25	12.00	2.00	1.00	1.00
Weight salt	0.0025	0.012	0.60	0.10	0.05	0.05
g mol salt	0.00006	0.00021	0.008	0.002	0.00045	0.0005

where the g mol salt is weight of salt divided by the molecular weight of the salt. If the value for 2% NH_4Cl is due to an experimental error and 8% is taken as the lowest válue that gives a positive increase, the g mol value becomes 0.008 for NH_4Cl. No reason is advanced for the plastic values for 2% and 4% NH_4Cl. These values were obtained repeatedly, as are recorded.

A tabulation of the change in the plasticity test values caused by the addition of alkaline and alkaline earth carbonates to kaolin is given as Table XIII. Lithium carbonate gives some plasticity at low concentrations and sodium carbonate at higher concentrations.

The action of a small amount of lithium carbonate gave an increase in the plasticity that was very nearly the same as that obtained with the chloride.

Salt	Gram molecules	Plast.	Gram molecules	Plast.	Gram molecules	Plast.
$LiCl$	0.00012	10	0.0003	16	0.0006	16
Li_2CO_3	0.00013	11	0.00033	12	0.00065	13

No such relationship was found for the other chlorides and carbonates studied. This uniformity in action of the chloride and the carbonate is found to be due to the formation of lithium hydroxide by hydrolysis and the loss of the hydrogen chloride and the carbon dioxide, respectively, during the drying of the clay slip on the water-bath. Mellor[1] points out that solutions of lithium chloride and carbonate lose hydrogen chloride and carbon dioxide respectively when heated. This is found to be true in the presence of a clay, as these materials when dried on a water-bath and remoistened are alkaline to litmus. As only the minimum amount of lithium carbonate that was used is clearly within the amount required to form a saturated solution with the few drops of water used to mold the clay at maximum plasticity, the other data are due to some of the lithium carbonate remaining undissolved.

TABLE XIII

Plasticity of Kaolin from Added Carbonate
Amount of Kaolin is five grams

% of salt	Plasticity					
	Na_2CO_3	K_2CO_3	$(NH_4)_2CO_3$	Li_2CO_3	$CaCO_3$	$MgCO_3$
0.00	4.5	4.5	4.5	4.5	4.5	4.5
0.20				11		
0.25					5	
0.50	15	7.5		12+	4.50	4.50
1.00				13		
2.00	13	7.0	6			4.00
4.00	18	7.0	6			

As sodium sulphate or material formed from sodium sulphate had been present as adsorbed impurities in some of the gelatinous aluminas used, the effect of the addition of a known amount on the plasticity of kaolin was obtained, Table XIV. The addition of a small amount of sodium sulphate to kaolin gives both an increased plasticity test value and a more plastic feel under the thumb.

The action of lithium as the sulphate is not marked, as 0.6% added salt gave to kaolin a plasticity test value of 6. One-half percent and one percent of lithium phosphate both gave the kaolin the plasticity test value of 14.

The change in plasticity of the kaolin brought about by the addition of sodium salts is

carbonate > sulphate > chloride.

The effect of the lithium salts should be given as

chloride = phosphate = carbonate > sulphate

rather than as

chloride > phosphate > carbonate > sulphate,

as the differences in the effect of the chloride, phosphate, and carbonate are smaller than the probable experimental error made.

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[1] "Treatise on Inorganic and Theoretical Chemistry," 2, 552.

Effect of Lithium Salts on Alumina and Silica.

Compounds of lithium had been found effective in increasing the plasticity of kaolin. Would such compounds when added to gelatinous alumina or gelatinous silica give to these materials the property of becoming gelatinous when remoistened after repeated alternate wetting and drying? To study the effect of electrolytes on gelatinous materials that are not clays, as this term is defined above, the plasticity test is not made the sole criterion. How plastic the material may be is of secondary importance to the presence or the absence of the property of plasticity of clay. To determine the presence or the absence of that property designated plasticity of clay, the following criterions are used:

(a) The powdered material, moistened to plasticity must not have the sandy or the bodyless feel of finely ground sand or the feel of a lack of mobility of a ground feldspar or alumina. The feel shall be that of a clay.

Table XIV

Plasticity of Kaolin with Added Sodium Sulphate
Amount of Kaolin is five grams

% salt	0	0.2	0.5	1	2	4	5	6	7	8
Plasticity	4.5	7	7.5	7.5	9	8.5	7	7.5	10	11

(b) The air-drying of the material, after it has been moistened to plasticity, must not give a cemented stone-like aggregate but one that may be abrased or crushed with approximately the same amount of pressure that is used to crush or abrase a clay.

(c) Repeated alternate air-drying and remoistening to plasticity must not give the sandy, bodyless feel of a sand or the lack of mobility of a feldspar or the stone-like texture of a cemented aggregate. There must be evidence of the presence of gelatinous material.

(d) The decantation of at least three-fourths of the supernatant liquid from the well-settled slip must not give a non-plastic mass. Repeated decantation or dialysis does not remove the plasticity of clay from natural clays.

(e) The air-dried material, previously molded when plastic, should give a characteristic action of a clay when placed in an excess of water. Such a characteristic action is that the surface or the entire mass becomes plastic, and that after an appreciable lapse of time the mass will disintegrate or spall off into a non-cohering mud.

When gelatinous silicas were heated on a water-bath with the amounts of lithium salts used with the kaolin, the silica was plastic so long as it was not heated to complete dryness. When the mass was dried and re-wet to plasticity, the material soon became sandy in feel and lost the power of bonding into a more cohering mass than of a finely ground sand when it was moistened with water. Lithium chloride does not give to gelatinous silica the property of again becoming gelatinous after drying on a water-bath and remoistening. The almost gritty feel of the material shows that there had been an enlargement of grain size and that the material was no longer of the proper texture to be classed as a clay.

When lithium chloride was added to a dialyzed gelatinous alumina, the rate of drying on the water bath was much slower than that of a blank run that contained no lithium salt. The dried material did not have a sandy feel of the characteristic feel of a finely ground alumina when it was remoistened to plasticity. This material was remoistened to a mass having the characteristic feel of a fat clay after the third alternate wetting to a slip, drying to a powder on a water-bath, and remoistening to plasticity.

One-half gram of lithium carbonate was added to gelatinous alumina (2 grams Al_2O_3) in a dilute slip and the material treated as follows:

a—Evaporated to dryness on a water-bath.

b—Moistened to plasticity and molded in the hand.

c—Heated one hour in a steam-bath.

d—Heated *1.5 hours in an air-bath at 110% with a final temperature of* 120°C.

e—Powdered and re-heated for 1 hour at 105°-110°C.

f—Moistened to plasticity and molded in the hand.

After this treatment, based on the first three criterions, the material had plasticity of clay and the gelatinous material would again take up water. Bischof[1] has evaluated plasticity by the ability of a clay to bond sand. This material was made into a slip and 5 grams of sandy open clay (plasticity test of 1/2) added, the slip evaporated to dryness, and the material moistened to plasticity and molded into a test ball, which was air-dried. When the air-dried test ball was placed under an excess of water, the test ball slowly spalled into a non-cohering mud. The water-soaked ball was not plastic but was readily kneaded into a plastic mass. This material was very similar in its action under water to the Albany slip clay and to the other natural clays that contain much carbonate. The Albany slip clay test balls spall in an excess of water but there is no softening of the ball into a plastic mass during the spalling. This dialyzed gelatinous alumina had been prepared from aluminum sulphate and contained materials adsorbed from sodium sulphate.

Although it was shown that lithium salts would hold alumina gelatinous when the *material* was *alternately* dried and *remoistened* to *plasticity* and that the commercial clays could be made more plastic through its addition, Professor J. Papish, using arc-spectra methods, could find no increase in the value of the lithium lines when the kaolin and the bond clays used by me were placed in the arc. This made it probable that these clays contained no lithium in any form and that their plasticity depended upon something else than lithium. *Lithium-containing* materials have been *found* in clay. Professor Lord[2] of Ohio State University writing on the presence of lithia in Ohio clays states: "the examination was made of a considerable number of

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[1] "Die feuerfesten Thone," 88.

[2] Trans. Am. Inst. Min. Eng., 12, 505 (1883-4).

samples and in every case the element was found, though in varying amounts to judge by the intensity of the spectrum." He reported "combined soda and lithia" where a modern analysis of clay reports "Na_2O."

Effect of a Combination of Electrolytes on the Plasticity of Kaolin.

The analyses of commercial clays report, as oxides, the presence of more than one alkali and alkaline earth metal. When more than one electrolyte was added to kaolin, the amount of plasticity obtained experimentally was found to agree with the amount calculated from the sum of their individual effects only when the salts added contained the same cation. Salts with the same anion but different cations or a combination of salts with no common cation or anion showed no agreement between observed and calculated plasticity. (Table XV). Also, it became apparent that the presence of a definite salt gave a specific action. When potassium chloride was added or the added salts were so chosen that a re-combination of the ions present would form potassium chloride, the plasticity found experimentally was less than that obtained by the action of the other salt alone on the kaolin, if the amounts present, or that could be formed, was shown in Table XI to depress the plasticity of kaolin. The actual or possible presence of ammonium chloride gave a similar result.

TABLE XV

Effect of a Combination of Electrolytes on the Plasticity of Kaolin

Amount of Kaolin is five grams

No.		Electrolytes added	Plasticity Calculated	Found
1	2% $CaCl_2$	4% $MgCl_2$	8.5	6
2	4% $CaCl_2$	2% $MgCl_2$	9.5	7
3	8% NaCl	1% LiCl	19.5	82
4	4% $Na_2\ CO_3$	2% NaCl	19	17.5
5	4% $Na_2\ CO_3$	2% NH_4Cl	24	5
6	4% $(NH_4)_2CO_3$	2% NH_4Cl	11	6
7	2% Na_2CO_3	6% NH_4Cl	8	3
8	2% $MgCO_3$	4% NH_4Cl	8	6
9	2% K_2CO_3	6% $CaCl_2$	12	5
10	2% Na_2CO_3	6% $CaCl_2$	20	120
11	1/2% Li_2CO_3	8% NaCl	26	200
12	2% K_2CO_3	2% $CaCl_2$ 4% $MgCl_3$	19	4.5

The addition of from 1/4% to 9% of lithium chloride (Table XI) had been found to give the same plasticity to kaolin. The addition of sodium chloride with lithium chloride or carbonate is now found to give a much greater plasticity than that which would have been predicted from the study of the effect of each acting alone. Also, it was found that the presence of lithium salts were not necessary, as the combination of sodium carbonate and calcium chloride produced a clay that had a very high plasticity test value and that worked well under the thumb.

It has been found in the study of the action of the chlorides on kaolin that only with the addition of the lithium salt had there been anything like a permanent change in the plasticity of the kaolin. With added sodium chloride the increased plasticity remained so long as it was present; with its removal, the kaolin regained its original plasticity. There seemed to be no evidence that if the kaolin took an appreciable amount of the salt by adsorption, by base exchange, or through any other cause, that the plasticity was affected by it. With the lithium salt the decantation of about 90% of the liquid that formed the slip, twice repeated, left the material with three times its original plasticity. Either the kaolin held the lithium, or some compound of the lithium, much more firmly than it could the sodium or some compound of the sodium; or the lithium chloride had brought about some change in the kaolin itself that was not brought about by the sodium salt. It is of course possible that both could have happened. One difference brought about by the addition of lithium chloride was that the water used for the disintegration of the test balls always had a decided turbidity. This turbidity was also found with added lithium carbonate. This turbidity was observed when the lithium salt was alone or used in combination with other salts. Lithium chloride did not act like sodium chloride because lithium chloride hydrolyzes and sodium chloride does not, and the removal of the water from the slip on the water-bath had removed some of the hydrogen chloride, as shown by the alkaline reaction of the slips that were reformed after a kaolin had been evaporated to dryness from a lithium chloride solution. The action of lithium chloride or of lithium carbonate should not be compared to the action of sodium chloride or kaolin; it should be compared to the action of a combination of salts on kaolin. The turbidity showed that a deflocculation caused by the presence of the lithium hydroxide had taken place. That deflocculation alone would not give increased plasticity had been shown by the failure of sodium hydroxide to make the alumina-silica mixtures into plastic clays. No. 10, Table XV had shown that it was possible to give a high plasticity to a kaolin without the presence of a lithium salt. Another reason had been found to explain the high results obtained when a small amount of lithium chloride or carbonate was added to kaolin or to a bond clay. The question remained,—were all the increased plasticity values obtained by the subsequent flocculation in the concentrated solutions produced in the final stages of the drying of the slip on the water-bath from an increased deflocculation that had taken place when the slip had been more dilute? If this was true, then the action of any material that would peptize a clay acting in the presence of a material that could flocculate it would give plasticity.

The Action of Flocculating Materials in Peptizing Solutions.

To investigate the effect on the plasticity of clay of the action of a flocculating material in a peptizing medium as an explanation of the cause of plasticity of clay, a salt was added to a clay slip that had been made alkaline through the addition of an alkaline hydroxide or carbonate. The slip was evaporated to dryness on a water-bath, the clay remoistened to plasticity and molded into a test-ball. The air-dried test-ball was allowed to disintegrate under water and the time of disintegration recorded as the plasticity of the clay.

The action of combined alkaline hydroxide and alkaline chloride on kaolin (Table XVI) beomes more evident when some of these and some previous results are recalculated in terms of a common unit, such as Na_2O. Table XVII gives such a recalculation.

TABLE XVI

Plasticity of Kaolin from a Flocculating Material in a Peptizing Medium
Amount of Kaolin is five grams

No.	% NaOH	% KOH	% Na_2CO_3	% KCl	% NaCl	Plasticity
1						4.5
2	0.8					8
3	0.8				4.0	13
4					4.0	4
5	0.4	0.6			0.8	5
6			0.5		0.1	12
7	0.8			1		3.5
8	1.5					7

TABLE XVII

Recalculated Kaolin Plasticity Values
Amount of Kaolin is 5 grams

No.	Material added	Na_2O equivalent	Plasticity
1			4.5
2	Sodium chloride	0.14%	6.5
3	Sodium carbonate	0.12%	15
4	Sodium chloride and carbonate	0.67%	12
5	Sodium hydroxide	0.6 %	8
6	Lithium chloride	0.15%	10
7	Lithium carbonate	0.33%	11
8	Lithium phosphate	0.09%	11

The comparison of the action of the chloride and the carbonate of sodium shows that the carbonate is twice as effective as the chloride and that the added effect obtained with the carbonate may be duplicated by allowing the chloride to react in an alkaline solution. Also, the deflocculating action of the dilute solution of sodium hydroxide alone and the later flocculating action of the concentrated solution obtained through the evaporation off of the water on the water-bath did not give as much increased plasticity as the use of a mixture of NaOH with the more powerful agent of flocculation, the chloride. Further, it had been found that 1 part of lithium chloride to 2000 parts of kaolin gave a plasticity of 6-1/2 and that 1 part to 1000 have a plasticity of

10. Now it is found that 1 part of combined sodium hydroxide and carbonate to 1500 parts of kaolin gives a plasticity of 12. The action of lithium was specific in producing plasticity only so far as lithium salts represented, under the conditions of the experiment, a flocculating material in a peptizing medium or a simultaneous peptizing and flocculating action.

It has been noted that one effect of the addition of lithium chloride to kaolin is the production of a turbid slip. It also was found that the addition of sodium hydroxide to a bond clay produced a turbid slip. When sodium chloride was used as the flocculating agent it was found more satisfactory to replace a small part of the sodium hydroxide with potassium hydroxide than to add a larger amount of sodium chloride. This did not give a clay with more plasticity but a clay that seemed more like a commercial clay under the thumb. In experiments on the effect of combined hydroxides and chlorides on No. 5 Kentucky bond clay the characteristics of the Bramlett clay were more nearly duplicated with the use of some potassium hydroxide with the sodium hydroxide. No. 10, Table XVIII in "feel" under the thumb and in the absence of excessive turbidity in the slip formed through the disintegration of the air-dried test-ball closely resembled the Bramlett clay. Including the amounts of Na_2O and K_2O reported in the analysis of this clay (Table I) and the amounts equivalent to the hydroxides and the chloride added, this synthetic clay would give on analysis, Na_2O = 1.3% and K_2O = 1.25% or less than the sum of Na_2O and K_2O in the Allen bond clay. Under the thumb and by the plasticity test, the Allen was the inferior clay.

TABLE XVIII

Action of Combined Alkaline Hydroxide and Alkaline Salts on No. 5 Kentucky Bond Clay

Amount of clay is five grams

No.	% $NaOH$	% KOH	% $NaCl$	% KCl	% K_2CO_3	Plasticity	Slip formed by plasticity test
1						15	Clear
2	0.8					50	Turbid
3	0.8		1.0			60	Turbid
4	0.4		1.0			34	Fairly clear
5	0.8			4		9.5	Turbid
6	0.8				2	12	Turbid
7	0.8			2	2	16	Turbid
8	1.0	10				19	Turbid 48 hrs.
9		1.0	2.0			18	Cleared in 24 hrs.
10	0.4	0.6	0.8			50	Clear as Bramlett slip

As noted above, the No. 5 Kentucky bond clay slacks with larger flakes than the Allen or the Bramlett and these larger flakes have plasticity, as they may be tamped together with a glass rod into a plastic mass. The No. 5 Kentucky bond clay acts as though flakes of higher plasticity were held together by a material of lower plastic value. The increase in plasticity in No. 10 was accompanied by the formation of a much smaller flake on the disintegration of the test-ball and these small flakes could not be readily tamped together to form a plastic mass. In all the tests on No. 5 Kentucky bond clay the presence of a small amount of potassium hydroxide seemed beneficial in that it prevented the extreme deflocculation caused by the use of sodium hydroxide alone.

The plasticity of No. 5 Kentucky bond clay was raised to 45 with the production of a very clear plasticity test slip and large size flakes on spalling, when with the addition of 0.8% of sodium hydroxide there was also added 0.2% of sodium acid sulphate. As well as having a high plasticity test this was also an exceptionally good clay under the thumb. The amount of sodium sulphate that would remain after the neutralization of the acid sulphate would be 0.74% and the amount of formed sodium sulphate would be 0.24%, which together would be equivalent to 3.4% Na_2O.

Effect of Simultaneous Peptization and Flocculation on Alumina and Silica.

Lithium salts have been shown to be effective in increasing the plasticity of kaolin, of bond clays, and of gelatinous alumina; but not to be effective in keeping gelatinous silica plastic. It has also been shown that the action of the lithium was not specific and that kaolin and bond clays are made more plastic through a combined peptizing and flocculating action. To determine the presence or the absence of that property called plasticity of clay in a gelatinous alumina and a gelatinous silica to which a lithium salt had been added, five criterias have been formulated. These criterias are now used to study the effect on gelatinous alumina and gelatinous silica of combined peptizing and flocculating materials.

Silica.—A gelatinous silica was prepared as described above from a water-glass solution and the sodium chloride washed out with a dilute sodium hydroxide solution. When slips of this material which were alkaline to litmus were evaporated to dryness the remoistened mass had the sandy, bodyless feel of a ground silica sand. With the addition of small amounts of either lithium chloride or of sodium chloride to the gelatinous material, one evaporation to dryness and remoistening to plasticity gave a material that had a slightly better plastic feel under the thumb than the material to which there had been no addition of an electrolyte but there was no evidence of the plasticity of clay. The texture was sandy; the bonding was that characteristic of ground silica. The presence of lithium or of sodium chloride does not prevent, and possibly hastens, the growth of grain size until the material is no longer of the proper texture to be classed as a clay, as the flocculation of gelatinous silica with a relatively large amount of sodium chloride and its subsequent removal by decantation gave, when the water was evaporated off, a material with a texture of a sand.

With the substitution of bivalent barium in place of the nonovalent sodium or lithium a plastic silica was obtained. In experiments with kaolin and with No. 5 Kentucky bond clay it had been found that the use of potassium hydroxide to replace some of the sodium hydroxide, while it did not give a higher plasticity test value, gave an artificial product more like a natural bond clay under the thumb than was obtained through the use of the sodium compound alone. To make a silica that was plastic this effect of the presence of potassium hydroxide was used.

To a gelatinous silica not completely freed from adsorbed sodium chloride and alkaline with sodium hydroxide some (0.2 g.) potassium hydroxide was added. After heating this material, which was in a dilute slip, for a short time on a water-bath a small amount (0.1 g.) of barium chloride was added and the solution evaporated to about 60 cc when it was found that flocculation had taken place. The solution was diluted to twice its volume. The precipitated material was well stirred, allowed to settle, and two-thirds of the supernatant liquid decanted. After a third washing by decantation, the diluted slip was evaporated to dryness, water added to form a dilute slip, and as much of the supernatant liquid as possible removed from the flocculated material. The decanted liquid had a slight opalescence and was alkaline to litmus. The silica was again evaporated to dryness. When moistened to plasticity, the material had the texture and feel of a kaolin. The characteristic bodyless feel of ground sand could not be detected. The material was air-dried and again moistened to plasticity. Twice the plastic mass was worked under water with a spatula and the supernatant water decanted. Twice the silica was moistened to plasticity and air-dried. When re-wet to plasticity the material was not sandy nor did it have the feel of a finely ground sand. After re-drying in the air, the material was placed under water where it softened and could be readily kneaded. Three days later the mass was twice wet to plasticity and dried. Six days of rigorous treatment had not made the material into a sand or silt. It was plastic, as it had retained the power of taking up water after modern drying and as it would soften under water to form a plastic mass.

Alumina.—If plasticity of clay is obtained whenever gelatinized materials are subjected to a simultaneous peptizing and coagulating action, then the plasticity of gelatinous alumina brought about by the addition of a lithium salt should also be brought about by the simultaneous action of an alkaline hydroxide and a flocculating salt. It is known that sodium chloride will flocculate colloidal alumina. It is thought probable, though not proven, that caustic soda in low concentrations will peptize alumina.

As the plasticity of kaolin may be increased by the simultaneous action of sodium chloride and sodium hydroxide and as it was not found possible to make a plastic silica through the addition of these materials, then if the silica was not the seat of the action, the alumina must have been and there was some concentration in the drying to a powder on the water-bath where the alumina in the kaolin was peptized by the alkali.

The peptizing action of dilute solutions of alkaline hydroxides on gelatinous alumina was studied through the action of amalgamated aluminum on distilled water, and on dilute solutions of sodium hydroxide. It was found that the action of the amalgamated aluminum on distilled water gave no peptized colloid that could be flocculated through the addition of sodium chloride to the clear liquid, that a N/20 sodium hydroxide solution acted upon the amalgamated aluminum to give appreciable amounts of peptized alumina that could be flocculated through the addition of sodium chloride to the clear liquid, but the amount of colloid so flocculated was relatively small when compared to the amount of alumina thrown out by the addition of hydrochloric acid to the liquid from which the flocculated colloid had been filtered, that in solutions the alkalinity of which was N/9, the amount of alumina held peptized and consequently could be flocculated through the addition of sodium chloride was relatively large when compared with the amount remaining after the flocculation by the chloride and which could be obtained from the filtered solution through the addition of hydrochloric acid to acid reaction and ammonium hydroxide to basic reaction. As alumina was peptized by the dilute solutions of sodium hydroxide and flocculated from them by sodium chloride, it is probable that the increased plasticity obtained from the simultaneous action of sodium hydroxide and sodium chloride on kaolin was due to their action on the alumina. Also, it should be possible to make alumina plastic through the use of these materials.

Through the use of gelatinous alumina prepared from the action of amalgamated aluminum on distilled water a material containing no adsorbed electrolytes was obtained. This was used to study the effect of added sodium hydroxide and added flocculating salts. When small amounts (0.05 and 0.1 grams) of sodium chloride was added to this gelatinous material made into a slip, the water evaporated off and the solid material remoistened to plasticity, the second evaporation to dryness gave a material that could not be molded as it had no coherence when moistened. A small amount of chloride acting alone did not keep the gelatinous alumina in a state in which it could adsorb water.

Gelatinous alumina was made more plastic than Florida washed kaolin and it continued to have the characteristic reactions of a clay after it had been eight times alternately dried on a water-bath and remoistened to plasticity under the thumb. It was prepared from the gelatinous alumina, made by the action of amalgamated aluminum on distilled water, to which was added 0.3 gm sodium hydroxide, 0.1 gm potassium hydroxide, 0.4 gm of sodium chloride, and that amount of water which would give a N/9 hydroxide solution. (As noted above the addition of the potassium hydroxide was thought to be beneficial in that it prevented the extreme deflocculation obtained by the sodium hydroxide alone.) The slip was heated for one hour on a water-bath, diluted to twice its volume and as much as possible of the supernatant liquid decanted off from the settled material. The sludge was evaporated to dryness on a water-bath. This material was then alternately molded into a plastic mass, wet to incipient stickiness and then again evaporated to dryness on a water-bath eight times. This material continued to have the properties of a clay in that it had under the thumb the feel of a clay. When dried to a powder on a water-bath it would again take up water and become plastic. When moistened to plasticity, molded into a sphere and air-dried, it softened slowly under water and could be easily molded.

That this was not a specific action of alkaline hydroxide and sodium chloride was demonstrated by the substitution of both barium chloride and sodium sulphate for the sodium chloride and the substitution of sodium carbonate for the sodium hydroxide.

The treatment of the material obtained through the simultaneous action of sodium carbonate and sodium sulphate was long and rigorous. Duplicate samples spalled slowly and were plastic one hour after being placed under water. (The plasticity test.) The previous treatment of this material had been as follows:[1]

a. Alternately moistened to plasticity, dried in the air, remoistened to plasticity, made into a slip, and re-evaporated to dryness.... 4 times.

b. Moistened to plasticity, dried in a steam-bath, made into a slip and the supernatant liquid decanted from the settled sludge.... 1 time.

The method used for the preparation of a plastic alumina through the addition of alkaline hydroxide and barium chloride was identical to that given for sodium chloride and alkaline hydroxide except for the use of 0.2 gram of barium chloride in place of sodium chloride. This material was eight times alternately wet to a plastic mass and then completely dried on a water-bath. After this treatment the molded air-dried material was easily kneaded into a plastic mass after it had been allowed to remain undisturbed for one-half hour under water. Some spalling had taken place in this time.

Conclusions and Summary

1. The cause of plasticity of clay is the formation in the moistened clay of a continuous gelatinous external phase through the action of water in making gelatinous the material that forms an enveloping surface around the non-gelatinous particles and aggregates present in the clay.

2. Plasticity of clay is not a property of a clay slip, unless the gelatinous envelopes surrounding the non-gelatinous particles and aggregates form a continuous external phase and the non-gelatinous particles and aggregates form the dispersed phase. Where the continuous external phase is a liquid and the dispersed phase is made up of particles and aggregates the surface of which is formed by a gelatinous envelope, the material has the property of viscosity. It does not have the property of plasticity of clay.

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[1] The increased plasticity of a clay on ageing is due to the gradual development of a gelatinous film as a result of repeated temperature and moisture changes.

3. The material that is capable of becoming gelatinous when it is moistened is maintained by a simultaneous peptizing and flocculation action which preserves the gelatinous envelope and hinders or prevents the change of its material into something that will not take up water and become gelatinous when moistened.

4. The presence of organic matter, of dissolved carbon dioxide, or of electrolytes in the supernatant water or in the clay itself is not the cause of plasticity of clay. Such materials are agents through the action of which a sufficient amount of material capable of becoming gelatinous when moistened is formed and once having been formed, by any agent, is preserved.

5. The relative plasticity of clay may be evaluated by the time taken for the continuous external phase formed by the cohereing gelatinous envelopes to be replaced through the formation of a continuous external liquid phase dispersing as the internal phase separated particles and aggregates each enveloped with gelatinous material.

6. Two methods are given for the measurement of the relative plasticity of clay: the one, using the air-dried material that had been wet to its highest plasticity as determined under the thumb, the other, using the material while it is plastic. The relative plasticity of some commercial bond clays as obtained by both methods is given.

7. The relative plasticity of clay obtained through the testing of the material that had been air-dried, after it had been moistened to its highest plasticity, is used in this paper as it seems to give results more in agreement with accepted relative plasticities of commercial bond clays than the alternate method. This test is: a small amount of the material to be tested, in a fine state of division, is moistened to its highest plasticity, as determined under the thumb, molded in the palm of the hand to a test-ball which is allowed to dry undisturbed in the air 16 to 24 hours. This test-ball is then so placed in an excess of water that the spalled particles may fall away from the disintegrating test-ball. The time in minutes required for the wasting away of the test-ball is recorded as the relative plasticity of clay for that material.

8. A dilute solution of sodium hydroxide peptizes alumina, but not all the aluminum present in the solution is so held, as the addition of sodium chloride will not flocculate all the compounds of aluminum in the liquid. The ratio of the amount held peptized to the total amount present was greater when N/9 sodium hydroxide acted upon amalgamated aluminum than when N/20 solution was used.

9. Gelatinous alumina and also gelatinous silica was made into a plastic material.

10. The criterions established to determine when a material had plasticity of clay were:—

a. The powdered material when moistened to plasticity of clay must have the characteristic feel of a plastic clay.

b. The air-drying of the plastic mass must not give a cemented aggregate.

c. Repeated alternate moistening to plasticity of clay and moderate drying must not remove the properties of bonding and of mobility when the material is remoistened to plasticity of clay.

d. When the material is made into a dilute slip and the supernatant liquid decanted from the well-settled sludge, re-drying and re-moistening to plasticity must not give a non-plastic mass.

e. The material, which has been molded into a test-ball, when moistened to plasticity of clay and then dried in the air, must not spall away at once like a finely ground sand when placed under water but form a mass that may be readily worked into a plastic mass or a surface layer of plastic material form on the test-ball or the entire undisturbed mass become plastic.

11. The constituent material of a clay and their structure are important only so far as kind of material and fissility may aid in the formation of a gelatinous material around the non-gelatinous particles and aggregates.

12. In actual clays the effect of humus must also be considered.

Acknowledgment

The clays used in this investigation were furnished by The Norton Company of Worcester, Massachusetts. My sincere thanks are tendered to Dr. Beecher, Director of the Research Laboratory and to Mr. Lamar, Chief of the Analytical Laboratory of The Norton Company, for their assistance. This work was inspired, its point of attack chosen, and its success due to Professor W. D. Bancroft of Cornell University, under whose direction it was done. Only the men who have worked under Bancroft know how inadequately any acknowledgment fits the facts. His great knowledge of Colloid Chemistry was the anvil on which this work was hammered out.

Cornell University.

HEAT OF WETTING OF CARBON BY BINARY LIQUID MIXTURES

BY F. E. BARTELL AND YING FU

In order to interpret data obtained in a study of heat of wetting of solids by a binary liquid system it is desirable to keep in mind the conditions which may exist during the process of adsorption. When an adsorbent comes into contact with a solution, its surface is exposed to both solvent and solute molecules. Theoretically, one of three things may happen: (1) the solute molecules may be adsorbed exclusively; (2) the solvent molecules may be adsorbed exclusively; or (3) both solute and solvent molecules may be adsorbed. In the latter case preferential adsorption of either solute or solvent may predominate. Suppose the adsorption of A from a binary mixture of A and B be exclusive. So long as there is sufficient A to cover the surface of the adsorbent, none of B will be adsorbed. If, however, one decreases the concentration of A until there is an insufficient amount of it to form a complete monomolecular layer on the surface of the adsorbent, some of B will then be adsorbed. If, on the other hand, both A and B are adsorbed, but to different degrees, the surface of the adsorbent will be covered by both components.

In the study of adsorption from solutions it has been customary to determine merely the change in concentration of the solution and to disregard the adsorption of the solvent, i.e., relative and not absolute adsorption values have been determined. Calculations have been based on the assumption that solute only was adsorbed. Volume changes due to adsorption of solute have been disregarded; this treatment may involve appreciable errors. There is evidence that both solvent and solute are always adsorbed. Bakr and McBain[1] using charcoal as adsorbent with toluene and acetic acid in the vapor phase found that both toluene and acetic acid were adsorbed and concluded that "true sorption of both solvent and solute is in accordance with the conception that toluene and acetic acid can replace each other in the adsorbed film." Attempts to determine absolute adsorption of solute from solutions have been made by Williams,[2] Osaka,[3] and Ostwald and Izaguirre,[4] but no really satisfactory method has been developed.

It is also customary in adsorption studies to disregard the question of fraction of the surface area actually covered by each of the components. It is our belief that information along this line will throw some light on the nature of adsorption and may eventually lead to a method for the determination of absolute adsorption of each component. It was the purpose of this investigation to obtain information bearing upon these problems.

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[1] J. Am. Chem. Soc., 46, 2718 (1924).

[2] Medd. K. Vetenskapsakad, Nobel-Inst., 2, 27 (1913).

[3] Mem. Coll. Sci. Kyoto Univ., 1, 257 (1915).

[4] Kolloid-Z., 30, 279 (1922).

It is well known that heat is evolved when a solid is wetted by a liquid. Disregarding the mechanism of wetting and assuming no chemical reaction to occur, it may be stated that the heat of wetting represents the decrease of total surface energy within the system. Since surface tension (or interfacial tension) is numerically equal to the free surface energy per unit area, Helmholtz's equation $E = S - T\, dS/dT$ may be applied where S is used to represent either the surface tension of the solid (or free surface energy per unit area) or the interfacial tension of solid against liquid and E the total surface energy per unit area.

When a solid (say of total area *a*) is immersed in liquid, it is assumed that no external work is done.[1] Suppose we let E_1 represent total surface energy of the solid and E_{12} the total interfacial energy of the solid-liquid system. Then, in accordance with the First Law of Thermodynamics, the heat evolved, —Q, is represented by the following expression:

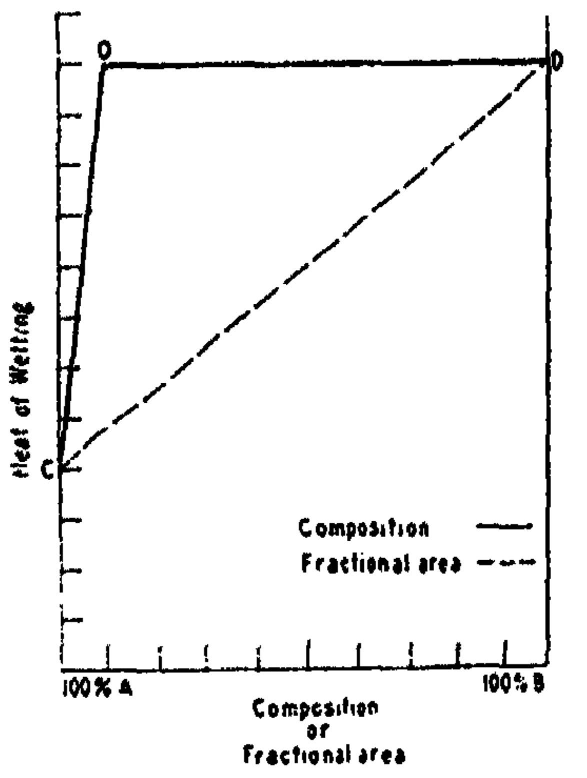

FIG. 1

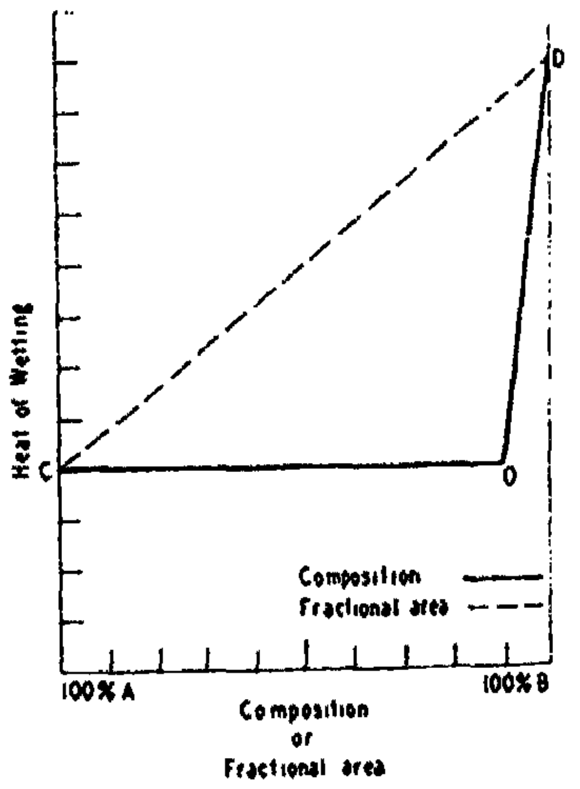

FIG. 2

$$-Q = a(E_1 - E_{12})$$

which in turn is equal to

$$a\left\{(S_1 - S_{12}) - T\left(\frac{dS_1}{dT} - \frac{dS_{12}}{dT}\right)\right\}$$

where S_1 and S_{12} refer to surface tension of the solid and interfacial tension of the solid-liquid respectively. Thus the heat of wetting is directly proportional to surface area. Since the interfacial tension values (S_{12}) for different liquids against a given solid are different,[2] the degree of wetting of a solid

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[1] It will be assumed that, when a solid is immersed in a liquid, the only appreciable energy change which occurs is that due to the substitution of a solid-liquid interface for a solid air interface; that any energy changes due to slight changes in concentration of solution or to the very small volume change within the system are of such a low order that the thermal changes observed are accurate within the limits of experimental error.

[2] Bartell and Osterhof: Colloid Symposium Monograph, 5, (1927).

by different liquids must be different and accordingly the heat of wetting for each of these systems must be different. This has been shown by the work of a number of different investigators.[1]

If both liquids are adsorbed from a binary mixture, the heat evolved must be due to the combined effect of both liquids. Should the wetting be by one component only, the presence of the other component would not appreciably affect the amount of heat evolved until the concentration of the more strongly adsorbed component should fall below a certain limit which corresponds to the formation of a complete monomolecular layer. In case both components are adsorbed, the heat evolved must be different from that evolved if but one is adsorbed. These relations can best be shown in Figs. 1-3.

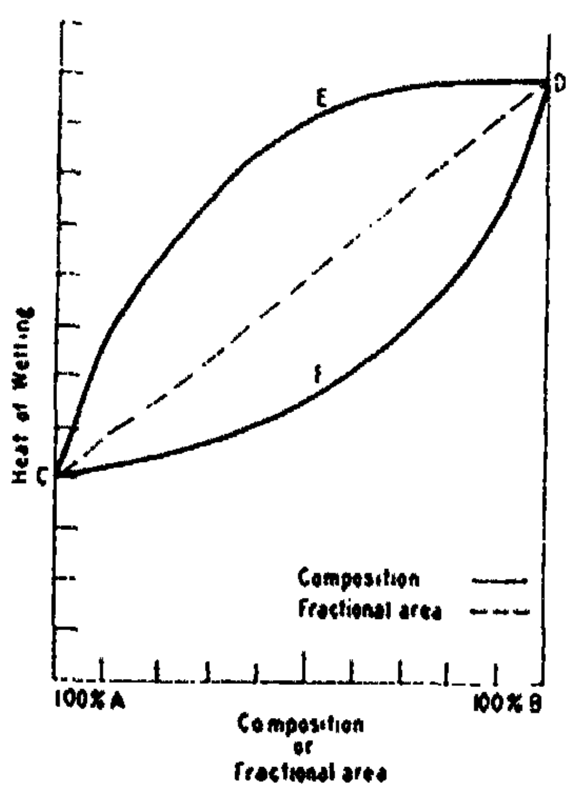

FIG. 3

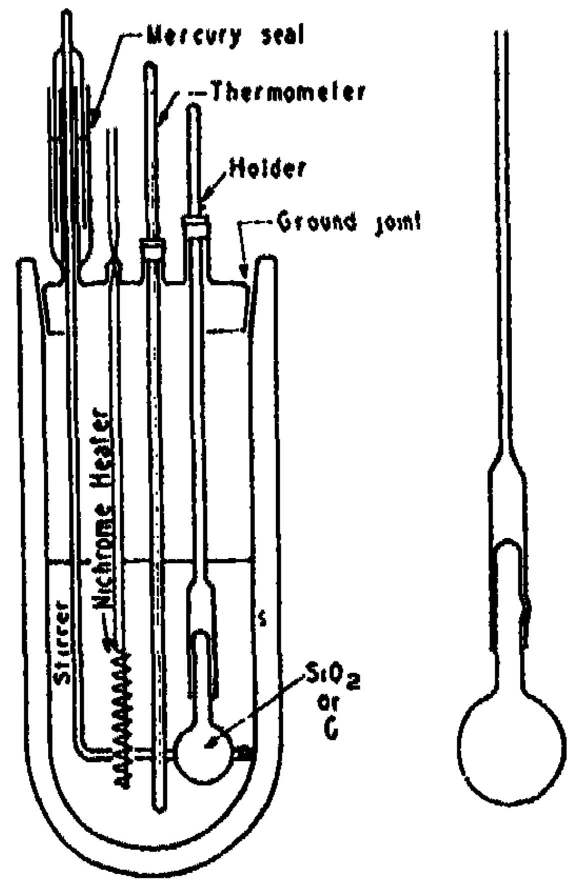

FIG. 4 a and b

Fig. 1 represents the case in which B only is adsorbed. As the concentration of the solution is decreased progressively from 100% B, the heat evolved is the same at each step until there is an insufficient amount of B present to form a monomolecular layer (point O). As the concentration of B is decreased further, the heat of wetting becomes progressively less until point C is reached, which corresponds to the heat of wetting of pure A. Fig. 2 represents the condition in which A is adsorbed exclusively from solution. Curve E of Fig. 3 represents adsorption of both components. B is indicated as being adsorbed preferentially throughout the entire range of concentration, while curve F represents the opposite case, i.e, A is preferentially adsorbed throughout.

If the two components are adsorbed in the same ratio as that of their composition in the solution (i.e., no preferential adsorption) the heat of

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[1] Grimm, Raudenbusch and Wolff: Z. angew. Chem., 41, 104 (1928); Patrick and Grimm: J. Am. Chem. Soc., 43, 2144 (1921); Gaudechon: Compt. rend., 147, 209 (1913); Herbst: Kolloid-Z., 38, 314 (1926); Andress and Berl: Z. physik. Chem., 122, 81 (1926).

wetting will change linearly with the concentration as is indicated by the dotted line, provided that a molecule of component A occupies the same area on the surface of the adsorbent as a molecule of component B. If the heat of wetting be determined for different concentrations of the solution, and if a horizontal line be drawn from a point on the experimental curve thus obtained to the dotted line, the point of intersection of the horizontal to the dotted line will then represent the ratio of the solid surface occupied by each component when the solution is of the composition given by the point on the experimental curve. The extent of deviation of the experimental curve from the straight line, measured horizontally, gives a relative measure of preferential adsorption at any particular concentration. Thus by measuring the heat of wetting of an adsorbent with solutions of any concentration we should be able to determine the fraction of the surface actually covered by each component, as also the effect of composition of the solution on the relative distribution of the two components on the surface of the adsorbent.[1]

Experimental

Materials: The carbon was prepared from Merck's pure cane sugar by charring it in a platinum dish. After it was charred, the carbon was ground in an agate mortar to a fine powder and heated to 1200°C for twelve hours in the absence of air. This carbon was then heated in a covered alundum thimble with a Meker burner for six hours with a limited supply of air. It was cooled in a desiccator and stored in a weighing bottle. Even though the carbon prepared in this manner might have contained a trace of impurities introduced by the flame rendering it unsuitable for exact work on adsorption of electrolytes, the amount of impurities was not sufficient to invalidate the

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[1] In the last two cases (Fig. 3) the situation is complicated by the fact that the surface areas covered by each of the molecules of different molecular species are *probably in most* cases not identical. Therefore, even though *no* preferential adsorption were to occur, the change of heat of wetting with composition will not be linear. The deviation of the curve from the straight line depends upon the relative area covered by the molecules (and also upon the difference in the heat of wetting values of the pure liquids). It is to be noted that these curves would *never* cross the straight line. In the liquids we have used, it is very improbable that the surface area covered by one kind of molecule is much greater than that covered by the other; consequently the actual deviation would not be great. If the experimental (composition-heat of wetting) curve were found to cross the straight line, it is very probable that preferential adsorption of each of the components occurred over some portion of the concentration range even though the point of inversion (i.e., the point of zero adsorption or no preferential adsorption) *may* not be identical with the point of intersection. A case of extreme preferential adsorption, that of alcohol-nitrobenzene, has been studied by C. K. Sloan of this laboratory, who found that both components were adsorbed by carbon even though the alcohol was much less adsorbed than the nitrobenzene. The concentration corresponding to zero preferential adsorption as determined by him was found to be very close to the concentration representing the point of intersection of the heat of wetting-composition curve with the dotted line. Therefore, the deviation of the actual (composition-heat of wetting curve in case of no preferential adsorption) curve from the straight line must be slight and for practical purposes we may consider the two curves identical. Unless the exact area occupied by the molecules of each component is known, such curves will only give a *qualitative* indication of preferential adsorption and can not be considered as representing a quantitative measurement. (The restriction made above will, however, not invalidate our discussion). Rigorously, the straight line in the figure represents the change in the distribution of the solid surface between the two liquids, whether or not the molecules of the one occupies the same area as the molecules of the other.

heat of wetting data. All liquids were purified by standard methods. The dilute solutions were made up by weight and the concentrated ones by volume.

Apparatus and method: The calorimeter used in this work was a Dewar flask with fittings similar to those used by Patrick and Grimm[1] (Fig. 4a). The cover of the flask was gas tight. Both the Beckmann thermometer and the heating coil were cemented into the cover with DeKhotinsky cement. The stirrer was mercury sealed. When the bulb containing the solid was set in position, the whole system was gas-tight; no evaporation was detected over a six-hour period. The carbon powder was sealed in a thin walled glass bulb which in turn was sealed to a glass holder (Fig. 4b). After the bulb had been introduced, the whole apparatus was placed in a felt jacket. The liquid was stirred continuously until the temperature remained constant for at least twenty minutes. This procedure is important; otherwise it is very dif-

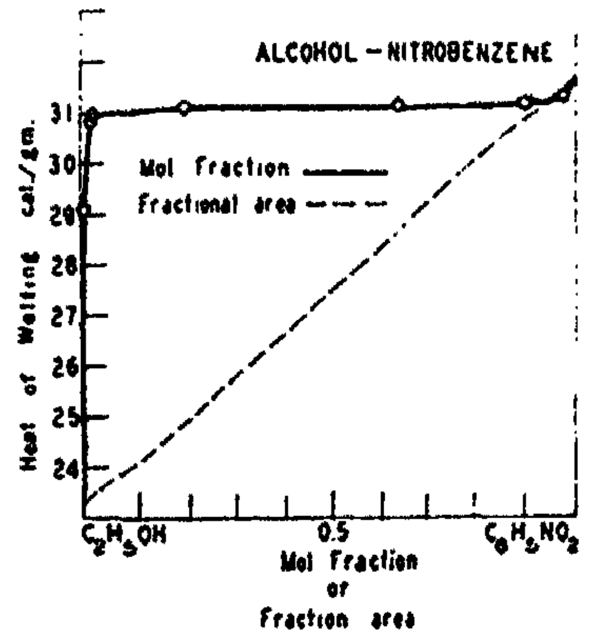

Fig. 5

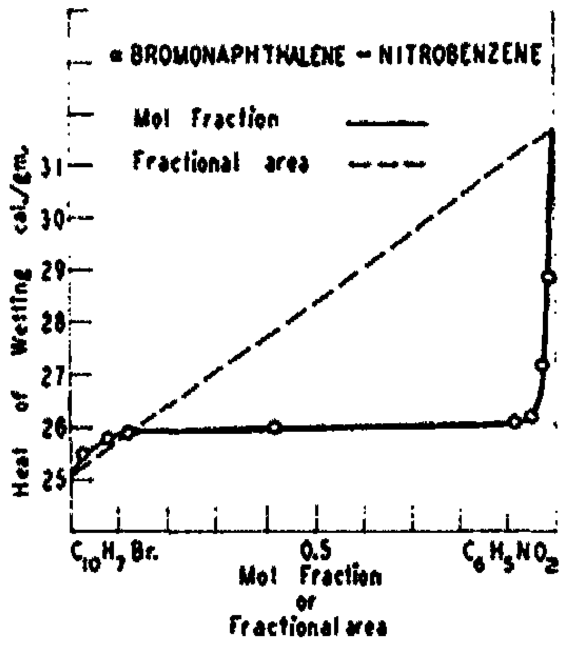

Fig. 6

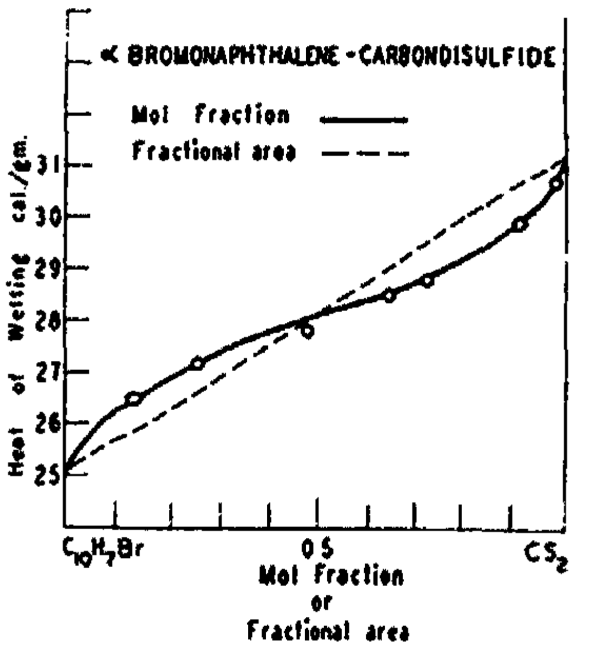

Fig. 7

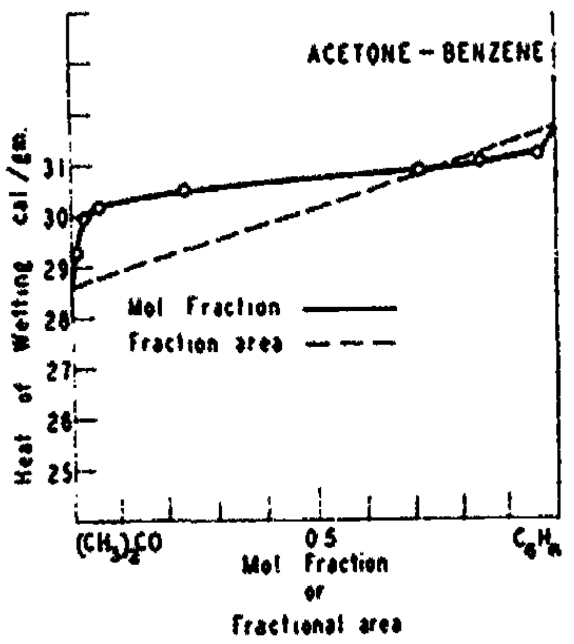

Fig. 8

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[1] J. Am. Chem. Soc., 43, 2144 (1921).

ficult to obtain uniform results. The bulb was then broken by pushing it gently against the wall of the calorimeter, and the change in temperature was noted. Just before the bulb was broken, the temperature external to the calorimeter was raised slightly (about 0.5°C) so that the temperature of the liquid after wetting and that of the surroundings was the same, heat loss was thus minimized. With some practice it was possible to maintain the temperature within the calorimeter (after wetting) constant for at least ten minutes. In all cases the calorimeter temperature reached the maximum within two minutes after the bulb was broken and remained constant for five or six minutes. This temperature reading was taken as the final reading. The heat capacity of the calorimeter together with that of the solid was determined by adding a definite amount of electrical energy to the system and noting the temperature rise. In some cases no attempt was made to equalize the calorimeter and room temperatures, but instead, thermometer readings

TABLE I

Heat of Wetting of Carbon with Binary Mixtures

1. Benzene-Acetone

Mole percent of C_6H_6	Heat per gm. carbon
0.0	28.6 cal
1.48	29.3
3.00	30.0
6.06	30.2
23.62	30.5
71.4	30.9
84.1	31.0
96.6	31.2
100	32.7

2. Alcohol-Nitrobenzene

Mole percent of alcohol	Heat per gm. carbon
0.0	31.7 cal
2.6	31.3
10.0	31.2
36.2	31.1
80.7	30.9
98.1	30.8
99.5	29.1
99.7	27.8
99.8	26.5
100	23.3

3. α-Bromonaphthalene-Carlon disulphide

Mole percent of CS_2	Heat per gm. carbon
0.0	25.1
12.8	26.5
25.2	27.2
47.6	27.8
64.4	28.5
72.8	28.8
91.5	29.9
98.0	30.7
100	31.2

4. α-Bromonaphthalene-Nitrobenzene

Mole percent of nitrobenzene	Heat per gm. carbon
0.0	25.1
2.7	25.5
8.1	25.8
12.3	25.9
41.8	26.0
92.3	26.1
96.0	26.2
97.8	27.2
99.0	28.9
100	31.7

were taken at fifteen second intervals, and corrections for heat loss were made by applying White's[1] formula. The two methods gave close agreement. In order to make sure that no evaporation of liquid occurred, the heat capacity of the system was determined at two hour intervals. Identical results were obtained in every case.

The results for four binary liquid systems are given in Table I, and are plotted in Figs. 5-8.

Discussion

From the data obtained two interesting facts are noted. The first is that neither component is adsorbed exclusively at any concentration, and the second is that "positive" adsorption of each liquid occurs over a certain range in each of the systems, the degree of adsorption of each component being dependent upon the concentration of the solution.[2] It thus follows that the usual method of measuring amount of adsorbed solute is not strictly accurate since the usual assumption regarding the non-adsorption of the solvent is not justified. It is also evident that the determination of surface area of adsorbents by adsorption experiments, as used by Paneth and Vorwerk,[3] Paneth and Radu,[4] and Garner, Knight and McKie[5] will most probably give low values, even in those cases where the adsorption is not affected by the hydrogen ion concentration of the solution, because allowance was not made for the adsorption of the solvent.

If it be considered that surface tension, or interfacial tension, is the determining factor in adsorption, and if Gibbs' theorem can be rigidly applied to solid-liquid interfaces, we have for a system containing an ideal solution,

$$u_1 = -(dS_{12}/dF_1) = -1/RT\, dS_{12}/d\log c_1$$

where u_1 is the excess of component 1 at the interface, F_1 is the chemical potential of component 1 and c_1 its concentration in the bulk of the solution. Since the adhesion tension A is given by the equation

$$A_{12} = S_1 - S_{12}$$

we have at constant temperature,

$$dA_{12} = -dS_{12}$$

as the surface tension of the solid S_1 is a function of temperature only. The formulation

$$u_1 = 1/RT\, dA_{12}/d\log c_1$$

expresses then the relation of adhesion tension to adsorption,[6] that is, the constituent which raises the adhesion tension of the solution against the

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[1] J. Am. Chem. Soc., **48**, 1147 (1926).

[2] This conclusion has since been confirmed by adsorption experiments carried out in this laboratory by the interferometric method.

[3] Z. physik. Chem., **101**, 445 (1922).

[4] Ber., **57**, 1221 (1924).

[5] J. Phys. Chem., **31**, 641 (1927).

[6] Bartell and Sloan: J. Am. Chem. Soc., **51**, 1643 (1929).

solid will be positively adsorbed. It is well known[1] that for many solutions the concentration-surface tension curve has a minimum point. By analogy, it is reasonable to expect the interfacial tension curve for solid-liquid systems to exhibit a similar relationship. Likewise, a maximum point in the adhesion tension concentration curve might be expected. It follows then that positive adsorption of both components may take place. It was found experimentally,[2] however, that in some systems which showed "positive" adsorption of both components, no maximum point existed on the adhesion tension-concentration curve. Letting c represent the concentration of the component with the higher adhesion tension, $dA_{12}/d\log c$ was found to be always positive.[3] As both R and T are positive quantities, u_1 should necessarily be positive throughout the whole range of concentration. This was found to be contrary to fact. It thus follows that adsorption of liquids from a binary mixture on a solid surface can not be completely accounted for by the interfacial tension-concentration relationships alone. It should be remarked, however, that this is not a conclusive proof of the inapplicability of Gibbs' theorem as related to solid-liquid interfaces. It is well known that if a substance raises the surface tension of the solvent, the increase is usually very small. If a similar action occurs at a solid-liquid interface, the effect of the component with lower adhesion tension may be small when compared with that of the one having a higher adhesion tension. The method available at present for the measurement of adhesion tension may not be sufficiently accurate to detect the small increase of adhesion tension due to the addition of a second component, (but this is not believed to be the case.) Work is being conducted in this laboratory which will permit of more detailed discussion of this point later.

The above apparent anomaly, can however, be accounted for in another manner. For the sake of simplicity the process of adsorption from binary mixtures may be treated by the following thermodynamically identical process. Let the adsorbent be first added to the pure liquid A, and after equilibrium has been established, a small amount of liquid B, which has a lower adhesion tension against the solid than A, be added to the system. Liquid B will then displace a small amount of A from the solid surface and equilibrium will again be reached. The free energy changes accompanying the whole process are as follows:

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[1] Whatmough: Z. physik. Chem., 39, 129 (1902).

[2] Bartell and Miller: unpublished results.

[3] The adhesion tension values of the liquids used, against carbon, are approximately as follows:

Carbon disulphide = 89.5 Bartell and Osterhof
α-Bromonaphthalene = 89.2 " "
Benzene = 81.1 " "
Nitrobenzene = 78.7 " " unpublished
Acetone = 71.0 Bartell and Fu, unpublished
Alcohol = 56.0 " " unpublished
Water = 54.7 Bartell and Osterhof

When the solid is wetted by liquid A, the solid surface, a, with a surface tension S_1, is replaced by an equal interface of interfacial tension S_{12}. The change in free energy at constant temperature and pressure is represented by

$$\int dF = a\int_{S_1}^{S_{12}} dS = a(S_{12} - S_1) = -a\,A_{(s-A)}$$

where $A(s-_A)$ is the adhesion tension of A against the solid. Suppose a small amount of B is then added. Adsorption occurs in finite time. At zero time, that is before the adsorption takes place, the concentration of A is c_2 and that of B is c_1. After adsorption, the concentrations are c_2' and c_1' respectively. We have then $c_2' > c_2$, and $c_1' \ll c_1$. The free energy change due to change in concentration is as follows:

$$\Delta F = \Delta F_A + \Delta F_B$$

where ΔF_B is the free energy change due to change in concentration of solution as a result of adsorption of B, and ΔF_A is that due to the desorption of A. As the process of adsorption involves a change in concentration of the solution, the change in free energy is represented by

$$\int_1^2 dF = \int_{P_1}^{P_2} v\,dp$$

where v is the volume and P the osmotic pressure of the solution. From this it follows[1]

$$\Delta F_B = \int_{P_1}^{P_1'} v\,dP = \frac{n}{N} RT \log_e \frac{c_1'}{c_1}$$

which is a negative quantity (n is the number of molecules of B removed from solution by adsorption). In a similar manner

$$\Delta F_A = \frac{n'}{N} RT \log_e \frac{c_2'}{c_2}$$

which is positive. It is not to be considered that n and n′ (the number of molecules of A restored to the solution) are identical unless the area occupied by a molecule of A is exactly the same as that occupied by a molecule of B.

Since c_1, the concentration of B, is very small at the start, a slight adsorption will correspond to a large relative change in concentration of B, while the concentration of A remains practically constant; consequently there is decided decrease in free energy due to the adsorption of B. When B displaces A from the surface there is a change in free surface energy, as the adhesion tensions of A and B are not the same. The decrease of free energy due to the adsorption of B is $(a'A_{s-B})$, and the increase due to the adsorption of A is $(a'A_{s-A})$, where a′ is the area on the adsorbent which was formerly occupied by A but is now taken up by B and (A_{s-B}) and (A_{s-A}) are the adhesion tensions of B and A respectively. The total change in free

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[1] For this treatment it is assumed that the solution is ideal, otherwise activity values should be used in place of concentration values.

surface energy is of course the algebraic sum of the two changes. If, as we have assumed, (A_{s-A}) is greater than (A_{s-B}), there is an increase in free surface energy due to the adsorption of B. Since the adsorption of a liquid of low adhesion tension from another of high adhesion tension is generally very slight,[1] this increase in free surface energy is small. Hence, it appears that a net decrease in free energy will result due to the different steps occasioned by the process of adsorption. It was found[2] that the adsorption of the component with low adhesion tension, B in the case in question, from A follows the Freundlich's equation. It follows, then, that at higher concentrations more B will be adsorbed than if but a trace of it were present. As one increases the concentration of B, the free energy decrease due to dilution of B through adsorption of it will become smaller and smaller, while on the other hand, the increase of free energy due to displacement of A becomes relatively greater. When these two quantities become of the same magnitude there will be no preferential adsorption of either component, i.e. the relative concentration on the surface of the adsorbent will be the same as that in the bulk of the solution. This is represented on the curves by the point where the experimental curve intersects the dotted line. If the concentration of B is further increased, the decrease in free energy due to dilution becomes smaller than the increase due to displacement. Hence, B will not displace A from the surface, and A will be preferentially adsorbed.

These curves also show that even though a liquid with low adhesion tension can displace one with higher adhesion tension, the adsorption of the former is usually very slight. If the two components have nearly the same adhesion tension, such as carbon disulfide and alpha bromonaphthalene, the preferential adsorption is low.

It is generally believed that heat of wetting is a measure of adsorbability. Berl and Wachendorff[3] concluded that less adsorption will occur from those solutions the solvent of which has a high heat of wetting, as the high adsorption of the one component will greatly decrease the adsorption of the other. Grimm, Raudenbusch and Wolff,[4] from a study of the heat of wetting of silica by alcohol-carbontetrachloride mixtures, also concluded the liquids showing a higher heat of wetting are more strongly adsorbed. While this generalization is true in most cases, it is by no means universal. Alphabromonaphthalene gives a comparatively low heat of wetting with carbon, but it is strongly adsorbed from nitrobenzene which has a much higher heat of wetting. This is really not surprising since the heat of wetting is a measure of the total surface energy change and not the free surface energy change. The latter is measured by the adhesion tension and this value for alphabromonaphthalene against carbon is high.

The curves tend to confirm the view expressed by Firth and Purse[5] that water in silica gel can be completely displaced by alcohol. Even though the

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[1] Bartell and Sloan: J. Am. Chem. Soc., 51, 1643 (1929).
[2] Bartell and Sloan: J. Am. Chem. Soc., 51, 1637 (1929).
[3] Kolloid-Z., 36, (Zsigmondy Festchrift) 36 (1925).
[4] Z. angew. Chem., 41, 104 (1928).
[5] J. Phys. Chem., 30, 617 (1926).

adhesion tension of alcohol against silica cannot be determined directly, the calculated value was found by us to be only a few dynes lower than that of water. As the two adhesion tensions approach each other, no one component will be predominantly adsorbed. If pure alcohol be continuously added and decanted off there is no reason to expect (from the present data) that the last trace of water cannot be completely displaced.

Summary

1. The heat of wetting of carbon with binary liquid mixtures has been determined with four different binary liquid systems.
2. A method has been proposed for the determination of the fractional part of total surface of adsorbent possessed by each of the two components.
3. It was found that in no case was either one of the liquids in a given system "exclusively" adsorbed. The component with the higher adhesion tension was adsorbed preferentially over a wide range of concentration while the component with the lower adhesion tension was preferentially adsorbed only at low concentrations, in small amounts, and over but a narrow concentration range.
4. The applicability of Gibbs adsorption theorem to solid liquid interfaces has been discussed and one of the discrepancies between theory and fact pointed out.
5. The thermodynamical relations which must exist in the process of displacement from the adsorbed state of one liquid by another were presented.
6. The general relationship which exists between heat of wetting and adsorption was discussed.

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THE RÔLE OF HYDROGEN ION CONCENTRATION IN THE PRECIPITATION OF CALCIUM AND MAGNESIUM CARBONATES[*]

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The pH value at which a solution of calcium acid carbonate precipitates out calcium carbonate depends on the concentration of total calcium, and a solution which contains calcium carbonate as a solid phase will begin to precipitate at a much lower pH value than one which does not contain the solid phase. Hence it was believed that, in view of the great importance of carbonate equilibria in natural waters, a quantitative study of the decreasing hydrogen ion concentration of pure solutions of calcium acid carbonate and of magnesium acid carbonate during precipitation would be of value.

Treadwell and Reuter[1] determined the solubilities of the acid carbonates of calcium and magnesium at various partial pressures of carbon dioxide, and found that, when the partial pressure was negligible, the calcium and carbon dioxide were present in solution in exactly the ratio to form calcium acid carbonate. In magnesium solutions, however, the magnesium present when the partial pressure of carbon dioxide was immeasurably small was in excess of that necessary to form magnesium acid carbonate with the carbon dioxide present in the solution. Greenfield and Baker[2] measured colorimetrically the pH values of water samples of known free carbon dioxide and calcium acid carbonate content. From the equilibrium equation for the first dissociation of carbonic acid, Greenfield and Baker deduced the following relation:

$$(\mathrm{H}^+) = \frac{3.5 \times 10^{-7}\,(\text{free } \mathrm{CO_2})}{(\text{bicarbonate } \mathrm{CO_2})} + 1 \times 10^{-8}$$

where (free CO_2) and (bicarbonate CO_2) are both expressed in parts per million. Auerbach and Pick[3] worked out the following equilibrium equation for the system, $\mathrm{CaCO_3{:}Ca(HCO_3)_2}$:

$$(\mathrm{H}^+) = \sqrt{\frac{k_1k_2a}{a + 2b} + \left(\frac{bk_1}{2a + 4b}\right)^2} - \frac{bk_1}{2a + 4b}$$

where *a* denotes the bicarbonate carbon dioxide and *b* the carbonate carbon dioxide in parts per million and k_1 and k_2 are the first and second dissociation constants of carbonic acid. Greenfield and Buswell[4] determined the pH value

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[**] From a dissertation presented by Mary Elvira Weeks in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Kansas. This work was begun under the direction of Professor Kemmerer at the University of Wisconsin and completed under Professor H. P. Cady at the University of Kansas. Professor Kemmerer has died since this manuscript was submitted for publication.

[1] Treadwell and Reuter: Z. anorg. Chem., 17, 199 (1898).

[2] Greenfield and Baker: J. Ind. Eng. Chem., 12, 989 (1920).

[3] Auerbach and Pick: Arb. kais. Gesundh., 38, 243 (1912).

[4] Greenfield and Buswell: J. Am. Chem. Soc., 44, 1435 (1922).

at which calcium and magnesium carbonates can be precipitated from solutions of their acid carbonates during electrometric titration with calcium hydroxide solution.

Apparatus and Materials

A solution of calcium acid carbonate was prepared by adding small portions of a saturated solution of calcium hydroxide (made from ignited calcium carbonate of C.P. grade) to a chilled, saturated solution of carbonic acid. Carbon dioxide from a cylinder was bubbled through the solution continuously to prevent it from becoming alkaline. The portion of the calcium acid carbonate solution to be used was filtered to make certain that no calcium carbonate was present as the solid phase. The carbon dioxide used in preparing the solution was bubbled through a solution of pyrogallol in sodium bicarbonate to remove oxygen. A portion of the carbon dioxide, collected over boiled water, when analyzed to test the efficiency of this method of removing oxygen, was found to contain only 0.19% of that gas. The oxygen dissolved in the calcium acid carbonate solution, as determined by the method of L. W. Winkler[1] amounted to 0.002 gram per liter. The following analytical results were obtained for the calcium acid carbonate solution:

MgO nil $\quad$ Cl^- nil
SO_4^{--} nil $\quad$ Fe 0.00036 gm. per l.

The magnesium acid carbonate solution was prepared in a similar manner from magnesium oxide of C. P. grade. The analysis of the MgO gave the following results:

CaO nil $\quad$ Cl^- 0.43%
SO_4^{--} nil $\quad$ Fe 0.25%

The mercury used in the calomel half-cell was distilled by the method of Hulett,[2] and the calomel was prepared from the C. P. grade by repeated washing with distilled water. The potassium chloride was re-precipitated by passing hydrogen chloride into a saturated solution of the C. P. salt, and subsequently decrepitating to expel hydrochloric acid and moisture. The voltage of the normal calomel electrode referred to the normal hydrogen electrode as zero was taken to be 0.2829 volt at 33° and 0.2848 volt at 25°.

The hydrogen electrodes were platinized in a 3% solution of platinum chloride containing 0.02% of lead acetate. Contrary to frequent statements in the literature, it was found that lead acetate is necessary for the production of a velvety deposit of platinum black and that, provided that the solution is kept scrupulously clean, such deposits are entirely satisfactory for hydrogen electrode measurements. This fact has been previously noted by Beans and Hammett.[3] The electrodes were platinized for eight minutes, with reversals of the current every thirty seconds. A fresh portion of the dilute sulfuric acid in which the electrodes were subsequently electrolyzed was used each time. Old deposits were always dissolved off with aqua regia before replatinizing.

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[1] Winkler: Ber., **21**, 2843 (1888).

[2] Hulett: Z. physik. Chem., **33**, 611 (1900).

[3] Beans and Hammett: J. Am. Chem. Soc., **47**, 1215 (1925).

The distilled water used in making the standard solutions was boiled vigorously for three hours, a slow current of carbon dioxide-free air being drawn through during the cooling. Standard N/44 solutions of hydrochloric acid and sodium carbonate were made up with this carbon dioxide-free water. An N/4.4 solution of hydrochloric acid was also prepared for titrating the samples taken from the magnesium acid carbonate solution. All standard solution were kept in bottles provided with soda-lime tubes and arranged so that burettes could be filled without access of carbon dioxide. The sodium carbonate used for making the standard solution and for standardizing the hydrochloric acid solution was prepared by heating chemically pure sodium bicarbonate for half an hour at a temperature of about 300°C. The indicators thymol blue-cresol red and bromphenol blue were prepared as recommended by Simpson.[1] The burettes were calibrated by the United States Bureau of Standards.

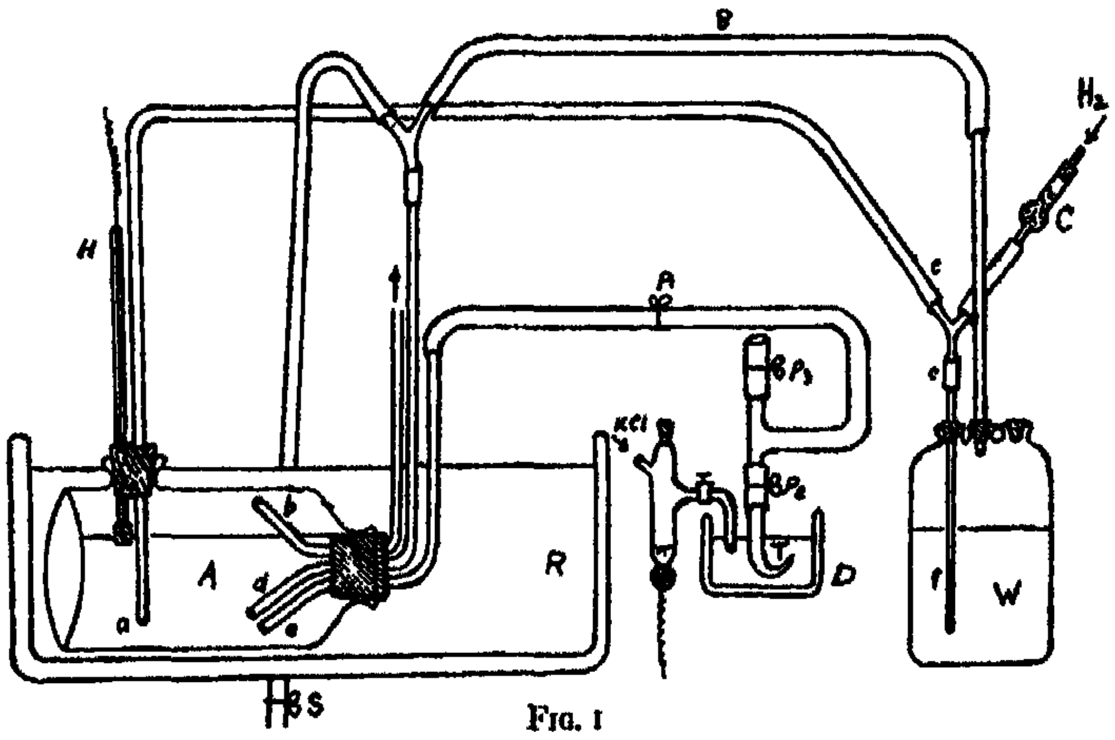

Fig. 1
A—Calcium Acid Carbonate Solution
d—Hydrogen Inlet; b—Outlet

A two-liter aspirator bottle *A*, fitted with rubber stoppers, hydrogen electrode and glass tubes as shown in Fig. 1, was used as reaction chamber. The stoppers were securely tied on to prevent accidental contamination of the calcium acid carbonate solution with water from the thermostat bath. The hydrogen electrode *H* made of 7 mm. Pyrex tubing was strong enough so that it could be slipped down through the snugly-fitting rubber stopper as the removal of samples for titration caused the level of the solution in *A* to fall. All rubber connections were boiled in sodium hydroxide solution to remove sulfides. Hydrogen, purified by bubbling through successive towers of alkaline pyrogallol, dilute sulfuric acid, distilled water and a calcium chloride tube *C* containing absorbent cotton, entered the reaction chamber through the glass tube *a*. Part of the hydrogen, after passing through the purifying train, bubbled through the two-liter Woulff bottle *W*, which con-

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[1] Simpson: Ind. Eng. Chem., 16, 709 (1924).

tained some of the same solution as that in *A*. By placing a 3-cm. length of capillary tubing inside the rubber tubing at each of the points *c*, and by slipping tube *f* up or down through the rubber stopper, the hydrogen could be made to bubble vigorously into *A* through the glass tubes *a* and *d* simultaneously, thus providing adequate stirring. The glass tube *b* served as an outlet for the hydrogen and for the carbon dioxide which was displaced from the calcium acid carbonate solution. The connection with the calomel cell was made by means of the glass tube *e* and the 7-cm. crystallizing-dish *D* containing a saturated solution of potassium chloride. The pinchcocks p_1 and p_2 on the rubber connections were kept closed while the level of the potassium chloride solution in *D* was adjusted to prevent diffusion into the tube *e*. This was accomplished by raising or lowering the platform support on which the dish *D* was placed. The pinchcock p_3 was used for permanently closing the rubber tube *r* after the glass tube *e* and the glass tip *T* had been filled by suction. Samples for titration were removed from *A* by temporarily closing the rubber tube *g* with a screw-cock, and allowing the hydrogen to force the solution out through the rubber tube *S*. The water thermostat *R* was held to within ± 0.°15 C by means of a mercury regulator.

The potential of the hydrogen electrode was read by means of a Leeds and Northrup student potentiometer and a standard Weston cell, which was kept packed in absorbent cotton. The electromotive force of this cell was found by comparison with a similar United States Bureau of Standards cell to be 1.01814 volts at 28.°5 C. A dial-form resistance box of ten thousand ohms in one-ohm steps was used in setting the potentiometer so that the portable galvanometer would give zero deflection. The sensitiveness of the galvanometer was sufficient to permit the use of the potentiometer to its full limit of accuracy.

Experimental Method

The hydrogen served the three-fold purpose of saturating the platinum black of the electrode, displacing carbon dioxide from the solution of calcium acid carbonate, and stirring the solution.

The changes in the composition of the solution were studied by means of frequent observations of the pH value and determinations of free and bicarbonate CO_2 and later, (after the solutions became alkaline to thymol blue-cresol red), of the carbonate CO_2. The free CO_2 was determined by the method of Seyler,[1] using a 100 cc. stoppered, volumetric flask with a bulb blown above the mark, as recommended by Tillmanns and Heublein,[2] to prevent loss of CO_2. Samples containing free CO_2 were collected directly in the volumetric flask and titrated immediately; those which were alkaline to thymol blue-cresol red were filtered rapidly through a dry filter, as a precipitate of calcium carbonate would interfere in the titration. Since the portion of the filtrate which first passed through the filter was rejected after being used to rinse the 100 cc. flask, the change of concentration due to ad-

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[1] Seyler: Analyst, **22**, 312 (1897).

[2] Tillmanns and Heublein: Z. Nähr. u. Genussm., **24**, 429 (1911).

sorption by the filter paper was considered to be negligible. The number of cubic centimeters of N/44 sodium carbonate solution required to produce the blue color of the thymol blue-cresol red end-point gives, when multiplied by five, the concentration of free CO_2 in parts per million. The bicarbonate CO_2 was determined on the same sample by the Hehner[1] method, the number of cubic centimeters of N/44 hydrochloric acid solution required to produce the bromphenol blue end-point giving, when multiplied by ten, the number of parts per million of bicarbonate carbon dioxide. The carbonate CO_2 content of solutions alkaline to thymol blue-cresol red was determined by titrating with N/44 hydrochloric acid solution until the blue color changed to yellow. The number of cubic centimeters of acid multiplied by ten gives the parts per million of carbonate carbon dioxide. The titration was then completed with bromphenol blue as indicator. The number of parts per million of bicarbonate carbon dioxide was calculated by subtracting from the total volume of acid used to produce the bromphenol blue end-point twice the volume of acid required for obtaining the thymol blue-cresol red end-point, and multiplying by ten.

The acidity of the filter paper was determined by titrating samples of distilled water before and after filtration, 0.05 cc. of N/44 sodium carbonate solution being required to titrate the acid dissolved from the filter paper. This would amount to 0.25 of a part per million of free carbon dioxide, which is less than the experimental error. The titrations of these samples of water were considerably more accurate than those of the highly-buffered samples of the calcium acid carbonate solution. Moreover, the rejection of the first portion of the filtrate made the error due to acid in the filter paper entirely negligible.

The pH value of the solution in the reaction chamber *A* was determined before and after the removal of each sample for titration and, when the pH was not constant, interpolation was made over the short time interval between readings. In the experiments which were made to test the Greenfield and Baker equation, the escaping gas was also analyzed at frequent intervals in order to correct the observed value of the pH for the partial pressure of carbon dioxide. The carbon dioxide was determined with the aid of an absorption pipette containing a solution of potassium hydroxide. Since, except for samples containing large amounts of free carbon dioxide, this correction was found to be within the experimental error, the gas was not analyzed in the later experiments, which were made primarily to determine the pH values at which precipitation would occur in solutions of various concentrations of total calcium, computed as the oxide.

Bovie and Hughes[2] state that when hydrogen electrodes are used continuously for a long time they may fail to function because of poisoning by mercuric ion, traces of which diffuse over from the calomel cell. The calcium acid carbonate solution in the reaction chamber *A* was tested, however,

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[1] Hehner: Analyst, 8, 77 (1883).

[2] Bovie and Hughes: J. Am. Chem. Soc., 45, 1904 (1923).

with ammonium sulfide solution and, even after runs lasting several days, no trace of mercuric ion was found. Whenever an unexplained fall in the apparent pH value of the solution was observed, the hydrogen electrode was replaced by a freshly-platinized one.

Experimental Data

As the hydrogen bubbled through the solution of calcium acid carbonate the pH rose rather rapidly until, after a few hours, the free carbon dioxide had been practically completely displaced. When the solution was very dilute, the only further changes were a very gradual loss of carbon dioxide at the expense of the bicarbonate, and a corresponding rise of the pH value. After the solution reached a pH value of 8 (i.e, became alkaline to thymol blue-cresol red), it consisted of calcium carbonate and calcium acid carbonate. With more concentrated solutions of calcium acid carbonate the solubility product of Ca^{++} and CO_3^{--} was finally exceeded, and calcium carbonate precipitated out.

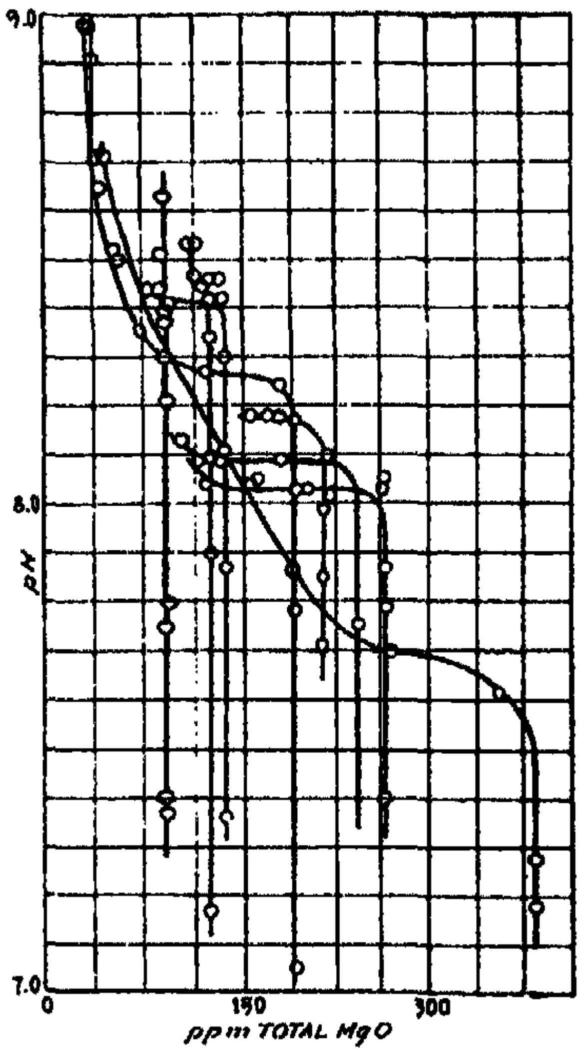

Fig. 2
30° C.

The pH value of the solution remained nearly constant during the precipitation, and increased again as loss of Ca^{++} became more gradual.

A comparison of the curves, (Fig. 2) shows that the pH value at which precipitation occurs is a function of the original concentration of the solution with respect to calcium oxide. To show this relation more clearly the pH values at which precipitation occurred have been plotted as ordinates against the corresponding concentrations of CaO as abscissae, (Fig. 3). The curve shows that the precipitation value of the pH is a linear function of the CaO concentration. Hence if the calcium oxide concentration of a given solution is known, the pH value at which it will precipitate out calcium carbonate may be calculated (at least within the range covered by these experiments) from the equation for the curve:

$$pH = -0.0028\ (CaO) + 8.79,$$

where (CaO) is expressed in parts per million, Table I.

In fourteen experiments the pH values were also calculated from the Greenfield-Baker equation. It will be noted that for high concentrations of carbon dioxide the observed values of the pH are lower than the calculated ones. This may be due in part to the inability of the hydrogen electrode to

TABLE I

Data for Fig. 3

p.p.m. CaO	Precipitation pH	p.p.m. CaO	Precipitation pH
123.3	8.44	239.3	8.10
133	8.41	270	8.10(?)
190	8.26	385	7.70
213.7	8.19	267.2	8.04

immediately adjust itself to the rapidly changing condition of the solution. The discrepancy is partly due also to the partial pressure of carbon dioxide above the solution but, even when the carbon dioxide in the escaping hydrogen was determined and the corresponding corrections were made, the pH values were still low. For small concentrations of carbon dioxide the observed pH values fall on the theoretical curve, the slope of which in this region is very great. In Table II the pH values were also calculated from the Auerbach-Pick equation for the carbonate-bicarbonate equilibrium. Here, again, the observed values are lower than the calculated ones; but, since the slope of the curve is very great, close agreement is not to be expected. The curves plotted from observed values lie close to the corresponding theoretical curves, Fig. 4.

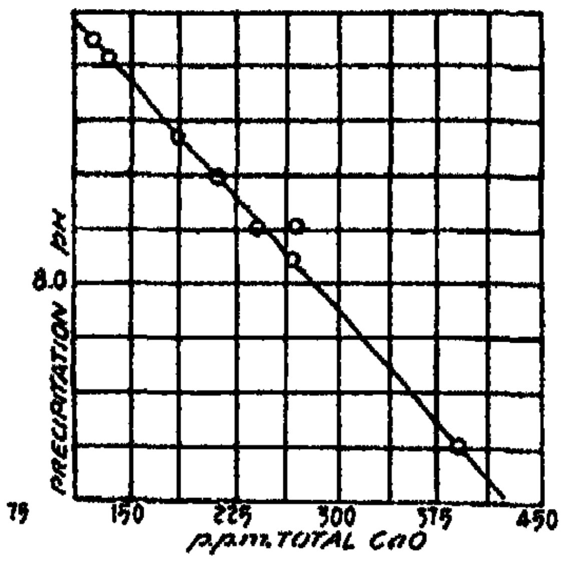

FIG. 3
33°C.

TABLE II

Temperature 33°C

Sample	Free CO_2 p.p.m.	Half Bound CO_2 p.p.m.	Total CaO p.p.m.	Carb. CO_2 p.p.m.	pH Observed	pH Calculated
1	118.85	103.90	132.3		6.12	6.56
2	80.85	100.45	128.0		6.55	6.73
3	56.5	104.25	132.8		6.75	6.87
4	38.60	104.5	133.1		6.86	7.02
5	16.15	103.65	132.4		7.36	7.34
6	3.50	105.1	133.9		7.87	7.75
7	0.00	105.45	134.4	0.00	8.14	8.00
8	0.00	100.35	132.55	3.70	8.30	8.49
9	0.00	95.65	134.3	9.70	8.42	8.93
10	0.00	94.1	131.7	9.10	8.46	8.91
11	0.00	66.48	91.08	5.10	8.41	
12	0.00	57.85	73.68	5.70	8.43	
13	0.00	55.35	70.5	2.10	8.44	

In the eleven experiments which furnished the data for Fig. 5 the thermostat was maintained at a temperature of 25°C. The equation for the linear curve expressing the relation between the concentration of total calcium

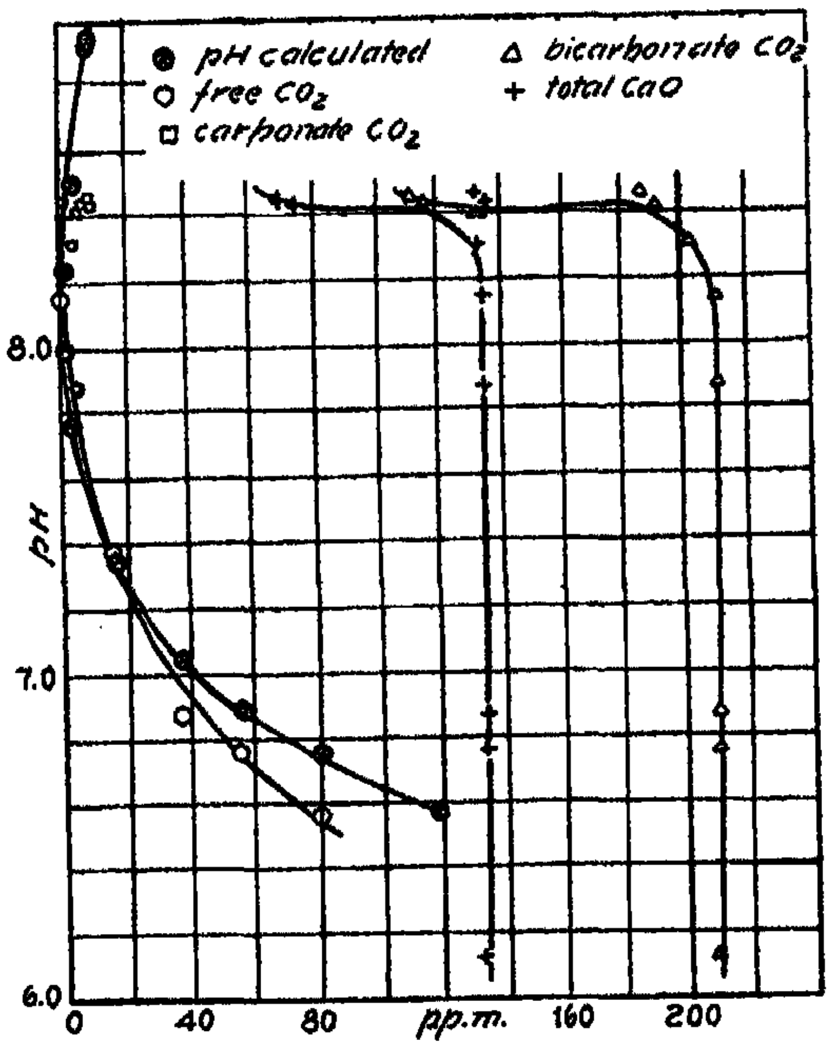

FIG. 4
33°C.

oxide and the precipitation value of the pH is:

$$pH = -0.0028\,(CaO) + 8.745$$

The pH value at which a calcium acid carbonate solution of given calcium oxide concentration precipitates calcium carbonate is increased 0.045 of a Sörensen unit for a temperature increase of 8°C. The temperature correction of the 100 cc. flask in which the samples were measured increases the values obtained at 33°C by one part per million, Table III.

TABLE III

Precipitation Data at 25°C

p.p.m. CaO	Precipitation pH	p.p.m. CaO	Precipitation pH
170.9	8.28	251.2	8.03
154.0	8.31	304.9	8.02
214.0	8.27	114.3	8.55
224.9	8.14	257.3	7.97
245.6	8.01		

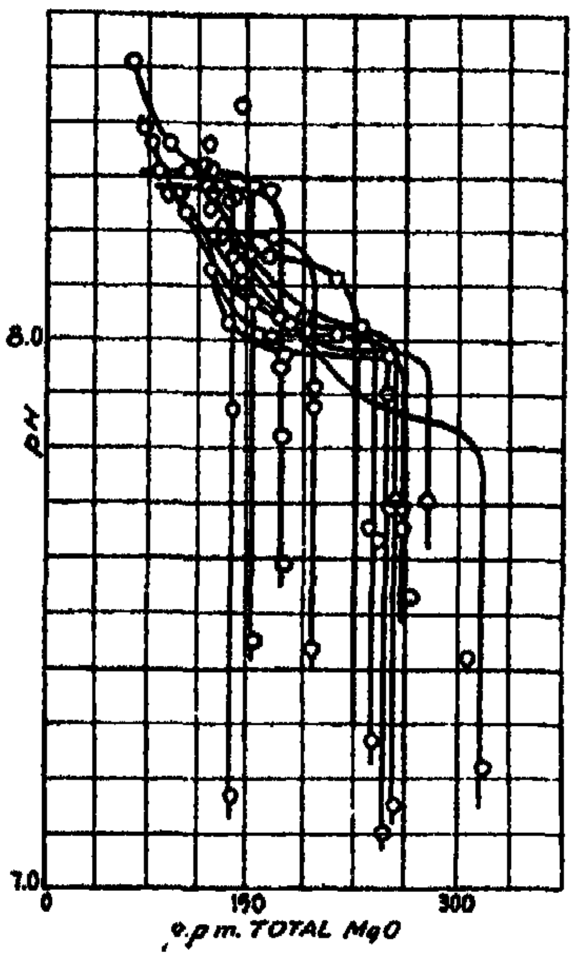

Fig. 5
25°C.

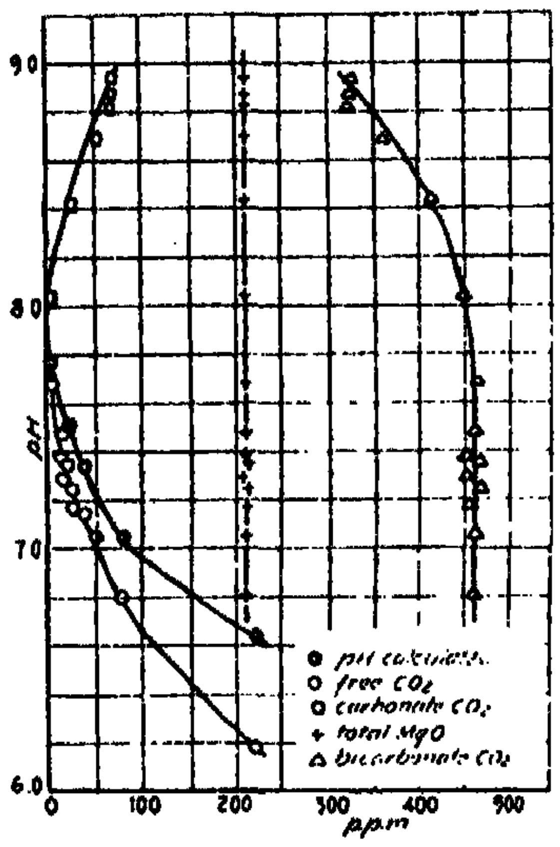

Fig. 6
33°C.

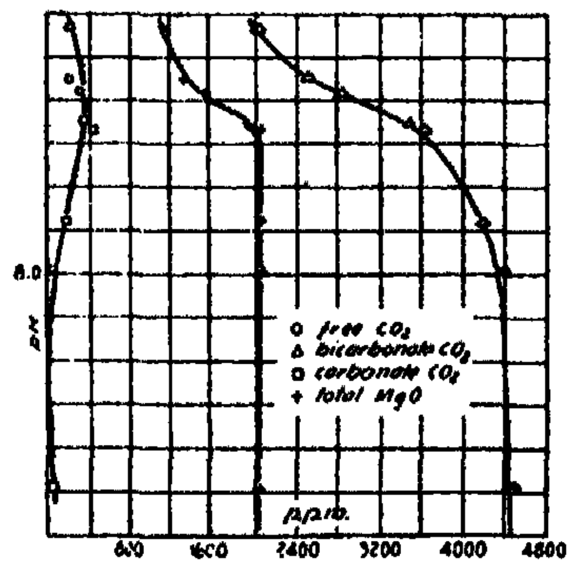

Fig. 7
33°C.

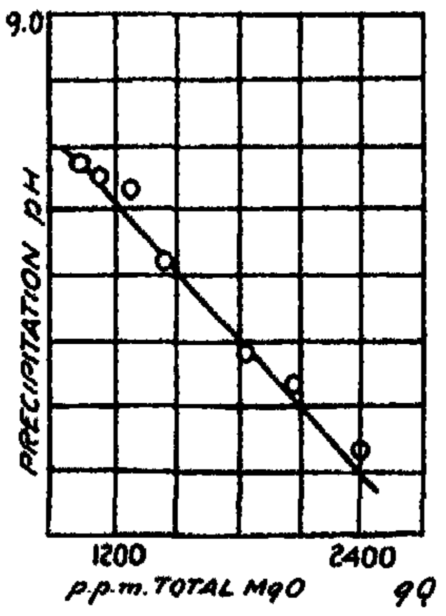

Fig. 8
33°C.

Precipitation of Magnesium Carbonate

When hydrogen was bubbled through a solution of magnesium acid carbonate, the pH increased rapidly as the free CO_2 was being displaced. With very dilute solutions such as the one used in Table IV the only further change was the loss of bicarbonate, with resulting increase of carbonate, carbon dioxide. In Table IV, carbon dioxide was very slowly bubbled into the magnesium bicarbonate solution and then displaced with hydrogen, Fig. 6.

TABLE IV

Sample	Free CO_2 p.p.m.	Half Bound CO_2 p.p.m.	Carb. CO_2 p.p.m.	Total MgO p.p.m.	pH Observed	ph Calculated
1		161.7	68.6	211.0	8.87	
2		not titrated	68.6		8.94	
3		160.15	68.8	209.7	8.83	
4		180.5	50.0	211.1	8.69	
5		206.25	24.8	211.6	8.43	
6		223.8	6.0	210.5	8.04	
7	6.40	229.65		210.4	7.68	7.78
8	11.65	225.95		207.0	7.38	7.66
9	16.0	226.15		207.2	7.29	7.58
10	23.85	228.0		208.8	7.17	7.47
11	not titrated	226.50		207.5	5.65	
12	221.0?				6.17	
13	80.2	228.65		209.5	6.80	7.04
14	47.55	230.00		210.7	7.05	7.24
15	35.45	not titrated			7.15	
16	25.05	232.10		212.6	7.24	7.46
17	21.15	232.55		213.1	7.35	7.51
18	16.45	230.7		211.3	7.48	7.58
19		176.85	29.4	189.0	8.60	
20		176.45	31.6	190.7	8.63	

TABLE V

Sample	Free CO_2 p.p.m.	Half Bound CO_2 p.p.m.	Carb. CO_2 p.p.m.	Total MgO p.p.m.	pH Observed	pH Calculated
1	144.55	2250.5		2062	7.51	7.61
2		2196	53	2060	8.01	
3		2093	154	2058	8.12	
4		1820	428	2059	8.33	
5		1744.5	371	1938	8.35	
6		1415.5	317	1587	8.42	
7		1252	247	1374	8.45	
8		1024	245	1163	8.57	

In Table V and Fig. 7 an inflection appeared in the carbonate carbon dioxide curve. With increasing pH value the carbonate increased at the expense of the bicarbonate carbon dioxide until precipitation of magnesium carbonate began. After this point the magnesium carbonate was apparently taken out of solution faster than it was produced by loss of carbon dioxide from magnesium acid carbonate. The rate of precipitation of magnesium carbonate from these supersaturated solutions is very great as compared with the slow transformation of magnesium bicarbonate into the carbonate.

In Fig. 8 is plotted the curve expressing the linear relation between the concentration of total magnesium oxide and the precipitation value of the pH, Table VI. The equation for this line is:

$$\text{pH} = -0.00033\ (\text{MgO}) + 9.12$$

Table VI

Data for Fig. 8

p.p.m. MgO	Precipitation pH	p.p.m. MgO	Precipitation pH
1846	8.48	1051	8.77
1303	8.73	2400	8.33
1458	8.62	2058	8.40
1141	8.75	2075	8.43

Discussion of Results

It is evident from a study of the curves that magnesium carbonate increases at the expense of magnesium acid carbonate more rapidly than does calcium carbonate at the expense of calcium acid carbonate. In solutions of calcium acid carbonate the bicarbonate carbon dioxide begins to decrease only when the precipitation value of the pH has been reached. In magnesium acid carbonate solutions, however, the bicarbonate carbon dioxide begins to decrease long before this precipitation value has been attained. The results are thus in accord with the previously mentioned observations of Treadwell and Reuter. These authors found that a saturated solution of calcium acid carbonate contains from 1.13 to 1.17 grams of calcium oxide per liter. The most concentrated solutions which we studied were therefore not more than half saturated. It is difficult to obtain accurate analytical results with solutions more concentrated than this because of separation of calcium carbonate as solid phase during titration. Magnesium carbonate, because of its greater solubility, precipitates out at much higher Sörensen values than does calcium carbonate.

Except for low concentrations of free carbon dioxide the pH values calculated from the Greenfield and Baker equation are not in accord with the observed values. It is possible, however, that in these acid solutions the hydrogen electrode was unable to adapt itself to the rapidly changing potential of the solution. The pH values calculated from the Auerbach-Pick equation are also not in accord with the observed results for solutions alkaline to thymol blue-cresol red. Greenfield and Buswell[1] found that when their solution of calcium acid carbonate, (the concentration of which was not definitely stated), was titrated with a one-tenth normal solution of calcium hydroxide, precipitation of calcium carbonate occurred at a Sörensen value slightly above pH 7. It is not to be expected that these two methods of precipitating calcium carbonate would yield the same result. Greenfield and Buswell observed that, even with their chemical method, several hours were required for complete precipitation; precipitation caused by bubbling hydrogen through the solution is still slower, however, requiring days instead of hours for completion.

Some of the calcium acid carbonate solutions showed a slight tendency to rise to an abnormally high Sörensen value just as precipitation was beginning, and in the magnesium acid carbonate solutions this behavior was well-defined. These high values were probably due to supersaturation, but a precipitate of magnesium carbonate was always plainly visible long before the pH had fallen to its normal precipitation value.

Summary

1. The pH values of solutions of calcium acid carbonate and of magnesium acid carbonate of varying concentration have been observed, the former at two different temperatures.

2. The precipitation value of the pH has been found to be a linear function of the concentration of the solution with respect to total calcium oxide or magnesium oxide.

3. Empirical equations for calculating the pH value at which a solution of known concentration of calcium oxide or magnesium oxide will precipitate have been given.

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[1] Greenfield and Buswell: J. Am. Chem., **44**, 1435 (1922).

THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF THE HALIDES OF CADMIUM

BY FREDERICK H. GETMAN

It was pointed out in a preceding paper[1] that, in consequence of the lack of dependable freezing point data for solutions of cadmium iodide, it was impossible to check the values of the activity coefficients derived from electromotive force measurements with those calculated from the freezing points of the same solutions. With a view to securing trustworthy data as a basis for further calculations of activity coefficients of cadmium salts, the following series of freezing point measurements were undertaken.

The modern methods employed for precise measurements of freezing points involve two fundamental improvements over the procedure followed by Raoult[2] and his contemporaries in their pioneer work in this important field. These improvements are (1) the substitution of thermocouples, or electrical resistance thermometers for the ordinary mercury thermometer, and (2) the determination of the actual concentration of the solution in contact with the solid solvent, when thermal equilibrium is finally established.

Apparently the first to replace the mercury thermometer by the thermocouple was Hausrath.[3] Other investigators who have employed thermocouples for precise freezing-point measurements are Osaka[4], Jahn,[5] Dixon,[6] Flügel,[7] Adams,[8] Harkins,[9] Randall and Vanselow,[10] and Hovorka and Rodebush.[11]

The platinum resistance thermometer was first employed for freezing-point determinations by Griffiths[12] and subsequently by Bedford,[13] Barnes, Archibald and McIntosh,[14] Elliott[15] and recently by Chadwell.[16]

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[1] Getman: J. Phys. Chem., 32, 945 (1928).

[2] Raoult: Compt. rend., 1878 to 1886; Ann. Chim. Phys., (5) 20, 27; (6) 2, 4, 8 (1880) to (1899).

[3] Hausrath: Ann. Physik, (4) 9, 522 (1902).

[4] Osaka: Z. physik. Chem., 41, 560 (1902).

[5] Jahn: Z. physik. Chem., 59, 31 (1907).

[6] Dixon: Proc. Roy. Soc. Dublin, 13, 49 (1911).

[7] Flügel: Z. physik. Chem., 79, 577 (1912).

[8] Adams: J. Am. Chem. Soc., 37, 481 (1915).

[9] Harkins: J. Am. Chem. Soc., 38, 2643-2717 (1916).

[10] Randall and Vanselow: J. Am. Chem. Soc., 46, 2418 (1924).

[11] Hovorka and Rodebush: J. Am. Chem. Soc., 47, 1614 (1925).

[12] Griffiths: J. Chem. Soc., 60 II, 251 (1891).

[13] Bedford: Proc. Roy. Soc., 83A, 454 (1910).

[14] Barnes, Archibald and McIntosh: J. Am. Chem. Soc., 27, 47 (1905).

[15] Elliott: J. Phys. Chem., 28, 611 (1924).

[16] Chadwell: J. Am. Chem. Soc., 49, 2795 (1927).

Although Roloff[17] appears to have been the pioneer in determining the exact composition of the solution in contact with the solid phase when equilibrium was attained, it remained for Richards[18] to point out the great superiority of this procedure over that followed by Raoult and his contemporaries. In all of the recent and more accurate measurements of the freezing points of solutions, Roloff's method with the experimental refinements introduced by Richards have been followed.

Apparatus and Materials

In the present investigation all temperatures have been measured by means of a platinum resistance thermometer in conjunction with a Mueller bridge and high sensitivity galvanometer manufactured by the Leeds and Northrup Company. Both bridge and thermometer were standardized by the Bureau of Standards. The thermometer had a resistance R_0, in melting ice of 25.471 international ohms, a fundamental interval, F, of 9.951 international ohms and a value δ in the familiar Callendar formula of 1.49. The bridge was certified to be accurate to within 0.00005 ohms under the specified conditions. During the entire series of measurements the variation in the temperature of the bridge was maintained within the limits guaranteed by the manufacturer to be without appreciable effect upon the accuracy of the resistance coils. By including in the circuit a suitable external resistance, the current flowing through the coil of the thermometer was reduced to approximately 3 milliamperes. With the precautions which have been taken to maintain constant conditions in the circuit, it is believed that the temperature measurements are accurate to 0.0005°.

The temperatures were calculated by means of the formulas developed by Callendar,

$$pt = \frac{100(R_t - R_0)}{F},$$

and

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right),$$

where R_t and R_0 are the resistances of the thermometer at the temperature t and in melting ice respectively, and where F is the fundamental interval, or difference between the resistance of the thermometer at 100° and at 0°. The true temperature, t, can be calculated from the so-called "platinum temperature," pt, by means of the second of the above formulas in which δ denotes the thermometer constant, 1.49.

A diagram of the freezing-point apparatus is shown in Fig. 1. An unsilvered Dewar Cylinder, A, 21 cm. deep and 6 cm. in diameter was employed as the freezing chamber. This cylinder was fitted with a rubber stopper through which passed the platinum resistance thermometer, B, a stirrer, C, a dropping funnel, D, for introducing the solution, and a pipette, E, for

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[17] Roloff: Z. physik. Chem., **18**, 572 (1895).

[18] Richards: J. Am. Chem. Soc., **25**, 291 (1903).

withdrawing samples of the solution for analysis after equilibrium had been established with the ice. The stirrer, C, consisted of an annular disc of brass perforated at regular intervals with circular holes. The stirrer and connecting stem were heavily plated with gold and the stem was fitted with a removable insulating handle. The tip of the pipette, E, was drawn out to a capillary to prevent the passage of small fragments of ice into the samples of solution withdrawn for analysis. The flattened silver tube containing the coil of the resistance thermometer was protected from any possible chemical reaction with the solutions by means of a thin coating of a cellulose lacquer known as "zapon." This lacquer was applied by dipping the tube in the liquid and, after allowing the excess of zapon to drain off, placing the tube in a vertical position, thus permitting the adhering film to dry slowly in the air. When perfectly dry, the tube was redipped, permitted to drain, and the adhering film of lacquer allowed to dry with the thermometer clamped in an inverted vertical position. This procedure insured the sealing of any minute pores in the film which might remain after the initial dipping. This method of treatment proved to be most satisfactory, the original coating having remained intact throughout the entire series of experiments. The freezing vessel, A, was placed co-axially within a large battery jar, F, which, when filled with a suitable mixture of ice and salt, served to maintain the temperature surrounding the cylinder, A, slightly below that of the equilibrium mixture in A. The temperature of the cooling mixture in F was read on a Beckmann thermometer, G. The outer vessel was insulated with a lagging of thick felt.

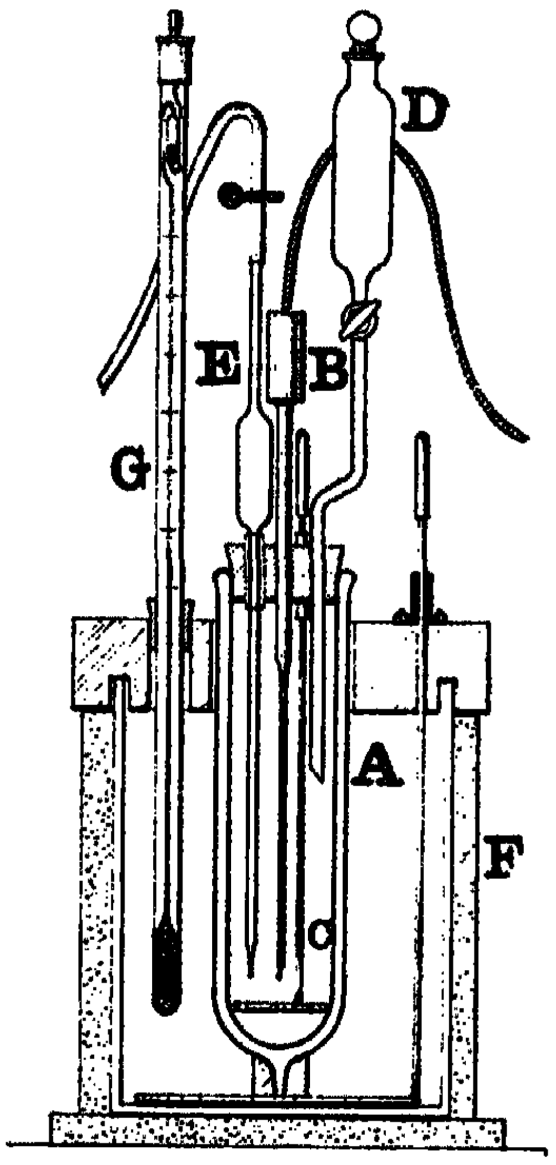

Fig. 1

Freshly-distilled conductivity water was employed in the preparation of the solutions and also in freezing the ice with which the solutions were to be mixed. The ice required for each series of determinations was obtained by freezing conductivity water in appropriate shallow trays in an electric refrigerator.

The salts employed in the preparation of the solutions were commercial products of chemically pure grade and were subjected to further purification by recrystallization before use.

Experimental Procedure

In carrying out a determination of the freezing point of the pure solvent alone, the outer vessel, F, was nearly filled with a mixture of ordinary finely crushed ice and water and the Dewar cylinder, A, put in place, as shown in Fig. 1. A portion of the pure ice was then crushed to a snow-like mass in a clean cloth bag which, after washing with distilled water, was introduced into A with sufficient cooled conductivity water to produce a mixture of slush-like consistence. Having assembled the apparatus as shown in Fig. 1, and having thoroughly stirred the contents of A, the resistance of the thermometer was measured at frequent intervals until it remained constant for at least twenty minutes. This constant value of the resistance was taken as R_0. The value of R_0 as thus determined was checked before each series of measurements and an extreme variation of less than 0.0004 ohm was noted during a period of over six months. The value of the freezing point of the solvent having been determined, a previously cooled portion of a concentrated solution of one of the salts under investigation was gradually introduced, with constant stirring, into the mixture of ice and water in A and a preliminary reading of the resistance of the thermometer taken. Sufficient common salt was now added to the cooling bath in F to insure a temperature several tenths of a degree below that of the equilibrium mixture in A. Readings were taken at brief intervals until the resistance remained unchanged for a period of fully fifteen minutes, when this constant value was taken as R_t. A 20 cc. sample of the equilibrium solution was then withdrawn by means of the pipette, E, and the content of cadmium salt determined. The analytical procedure adopted for the determination of the concentration of the solutions was to evaporate the solutions to dryness and then heat in an electric oven to constant weight. By adding successive portions of precooled solution and water the temperatures corresponding to other equilibrium mixtures could be determined in a similar manner. Through the exercise of care in the choice of the volume and concentration of the solutions added to the ice and water mixture, it was possible to effect an overlapping of the freezing point data in successive series of determinations, thereby checking the accuracy of the measurements. Owing to the hygroscopic character of the chloride and bromide of cadmium, considerable care was necessary in order to insure the removal of the last traces of moisture from the residues, in the determination of the concentration of the equilibrium mixtures.

Experimental Data

The values of the depressions of the freezing point of water produced by solutions of the chloride, bromide and iodide of cadmium, as calculated from the readings of the resistance thermometer, are given in the subjoined tables. In these tables, m denotes the concentration, expressed in mols of salt per 1000 grams of water, θ the depression of the freezing point of water in degrees Centigrade and θ/m the molal depression of the freezing point.

The molal depressions of the freezing point given in the foregoing tables are plotted against the corresponding concentrations in Fig. 2.

TABLE I

Freezing Points of Aqueous Solutions of Cadmium Chloride

m	θ	θ/m	m	θ	θ/m
0.0156	0.0743	4.758	0.2023	0.6733	3.329
0.0198	0.0871	4.392	0.2288	0.7516	3.285
0.0447	0.1822	4.071	0.3072	0.9517	3.098
0.0611	0.2377	3.893	0.3651	1.1161	3.056
0.0801	0.3000	3.744	0.5476	1.5549	2.839
0.1155	0.4155	3.599	0.6577	1.8194	2.766
0.1201	0.4287	3.571	0.7709	2.0849	2.705
0.1672	0.5764	3.447			

TABLE II

Freezing Points of Aqueous Solutions of Cadmium Bromide

m	θ	θ/m	m	θ	θ/m
0.0165	0.0683	4.148	0.3354	0.9358	2.790
0.2043	0.0951	3.913	0.4303	1.1149	2.591
0.0366	0.1367	3.736	0.4636	1.1850	2.556
0.0680	0.2377	3.497	0.5112	1.2944	2.532
0.0893	0.2901	3.248	0.5232	1.3083	2.500
0.1139	0.3683	3.233	0.5372	1.3528	2.519
0.1994	0.5931	2.974	0.5967	1.5004	2.514
0.2236	0.6586	2.945	0.6360	1.5933	2.505
0.2581	0.7368	2.855	0.6396	1.5886	2.484

TABLE III

Freezing Points of Aqueous Solutions of Cadmium Iodide

m	θ	θ/m	m	θ	θ/m
0.0104	0.0357	3.433	0.2548	0.5206	2.013
0.0211	0.0673	3.190	0.2702	0.5426	2.008
0.0323	0.0953	2.950	0.2782	0.5585	2.008
0.0468	0.1267	2.707	0.3277	0.6595	2.012
0.0699	0.1743	2.494	0.3377	0.6714	1.988
0.0822	0.2010	2.445	0.3620	0.7278	2.010
0.0874	0.2089	2.391	0.4263	0.8606	2.018
0.1075	0.2426	2.253	0.4808	0.9705	2.019
0.1412	0.2991	2.115	0.5039	1.0180	2.019
0.1732	0.3585	2.070	0.9847	2.328	2.36

Similar data for these salts as determined by Kistiakowsky,[19] Jones,[20] Jones and Chambers,[21] Chambers and Frazer[22] and Arrhenius,[23] are also plotted for comparison. Jones and his co-workers, as well as Arrhenius, having expressed the concentrations of their solutions in mols per liter, it was necessary, in order to compare their results with ours, to transform the concentrations tabulated in their papers to the molal basis. In this calculation use was made of the data compiled by Drucker[24] on the densities of the cadmium halides. It will be seen that the molal depressions of the more concentrated solutions, as determined by these earlier workers, are almost without exception greater than the corresponding depressions determined by us. It is believed that this disagreement is to be ascribed to the use of too cold a freezing mixture in the outer bath of the Beckmann apparatus which was employed in almost all of the earlier cryoscopic work.

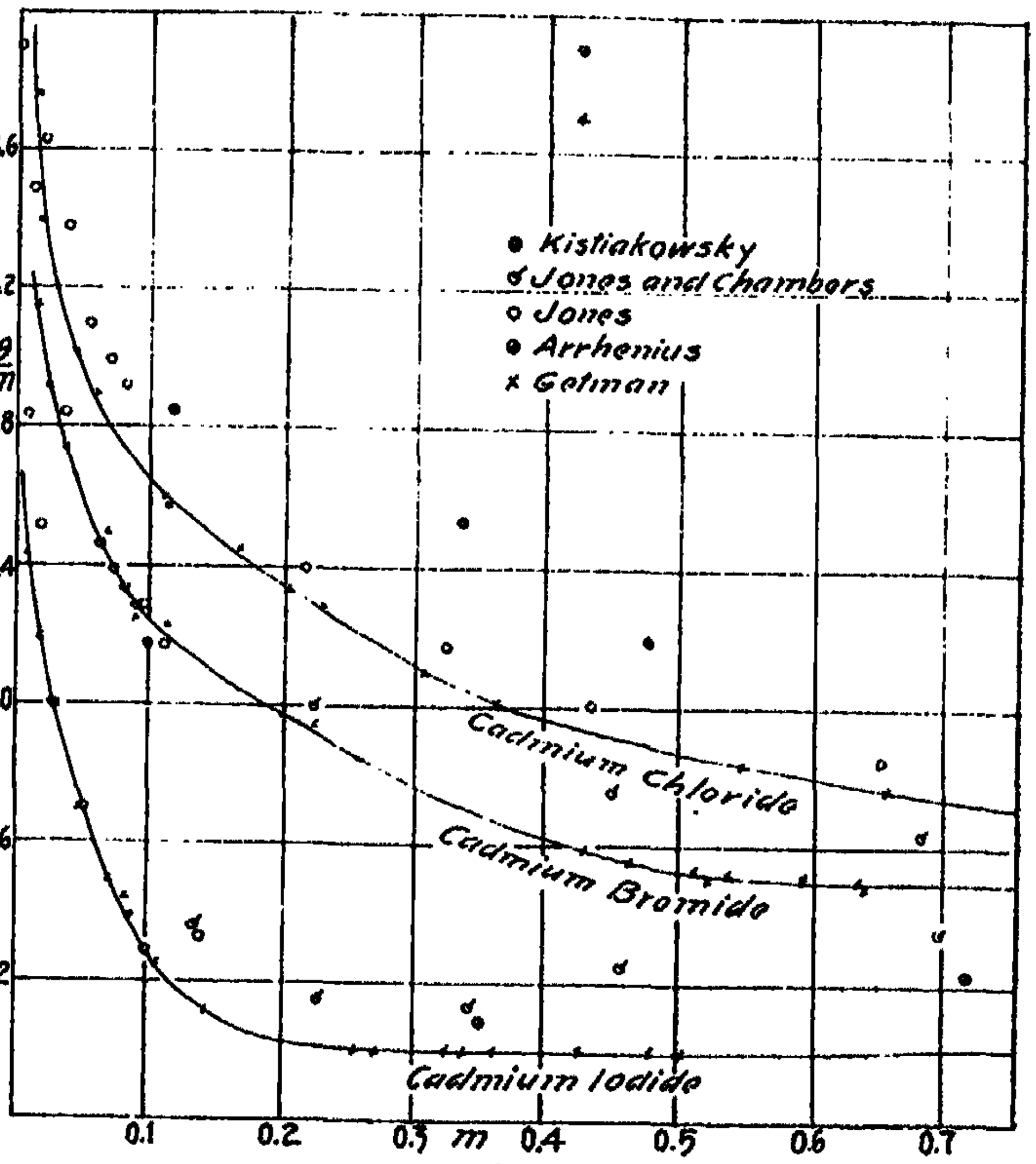

Fig. 2

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[19] Kistiakowsky: Z. physik. Chem., 6, 108 (1890).
[20] Jones: Z. physik. Chem., 11, 542-544 (1893).
[21] Jones and Chambers: Am. Chem. J., 23, 89 (1900).
[22] Chambers and Frazer: Am. Chem. J., 23, 512 (1900).
[23] Arrhenius: Z. physik. Chem., 2, 496 (1888).
[24] Abegg's Handbuch der anorganischen Chemie, 2, 442, 450, 455.

Calculation of Activity Coefficients

Lewis and Randall[25] have developed a formula for the calculation of the activity coefficients of electrolytes based upon the freezing point depressions, partial molal heat contents and heat capacities of their solutions. Unfortunately complete thermal data for the halides of cadmium are not as yet available and, therefore, we are obliged to content ourselves for the present with the calculation of what may be termed "tentative" activity coefficients, γ'. According to Lewis and Randall, γ' can be computed by means of the formula

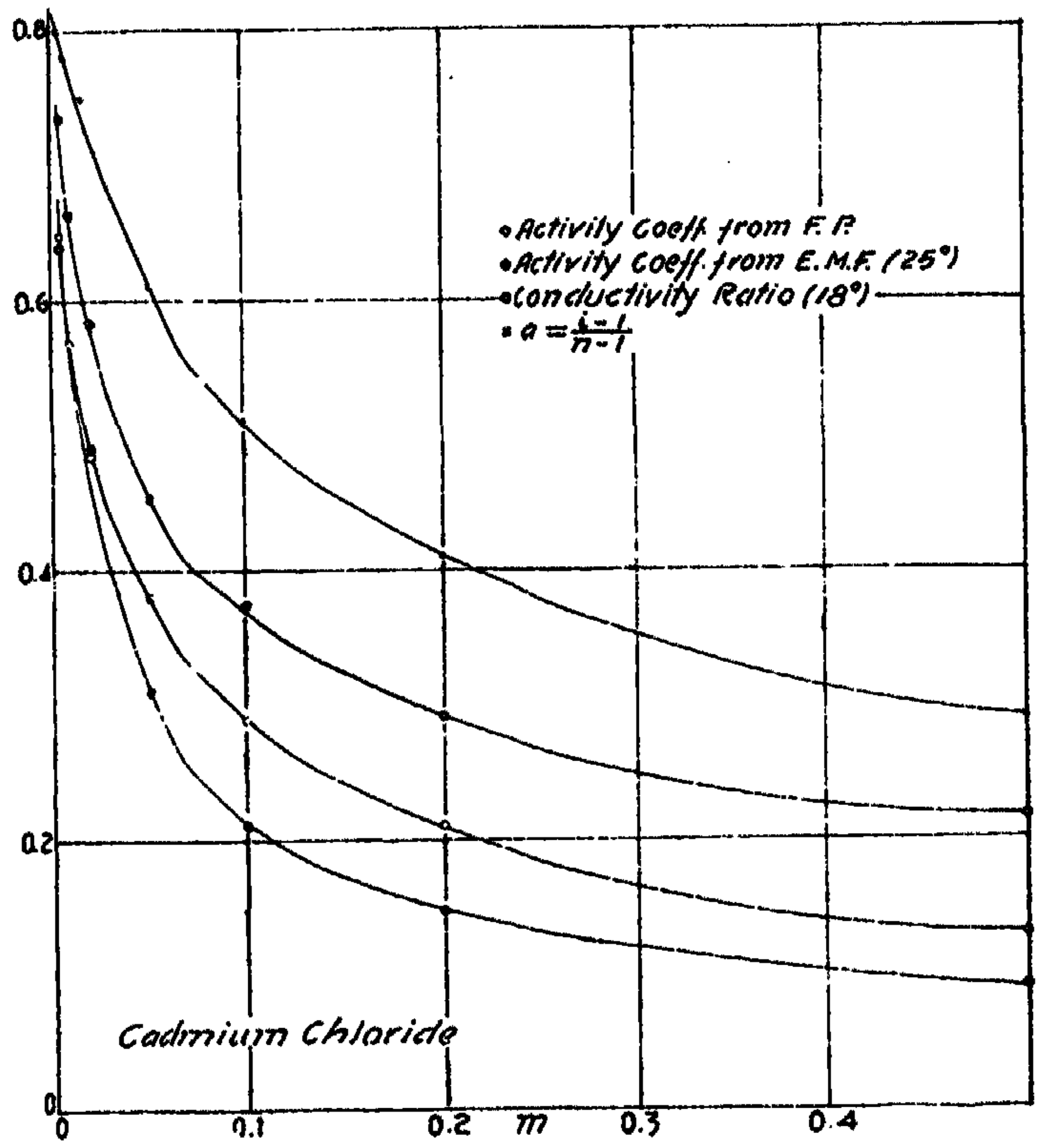

Fig. 3

$$\log \gamma' = \int_0^m - j\,d\log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m}\, d\theta, \qquad (1)$$

where θ is the molal depression of the freezing point, m the molal concentration, ν the number of ions into which the electrolyte dissociates, and

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[25] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances" Chapters XXIII and XXVII.

$j = 1 - \theta/1.858\nu m$. For solutions of all electrolytes below 0.01M, it has been shown by Lewis and Linhart[26] that

$$j = \beta m^{\alpha}, \qquad (2)$$

where α and β are constants derived by plotting log j against log m and noting that α is the slope of the line and that log β is the intercept on the axis of log j. It follows, therefore, that

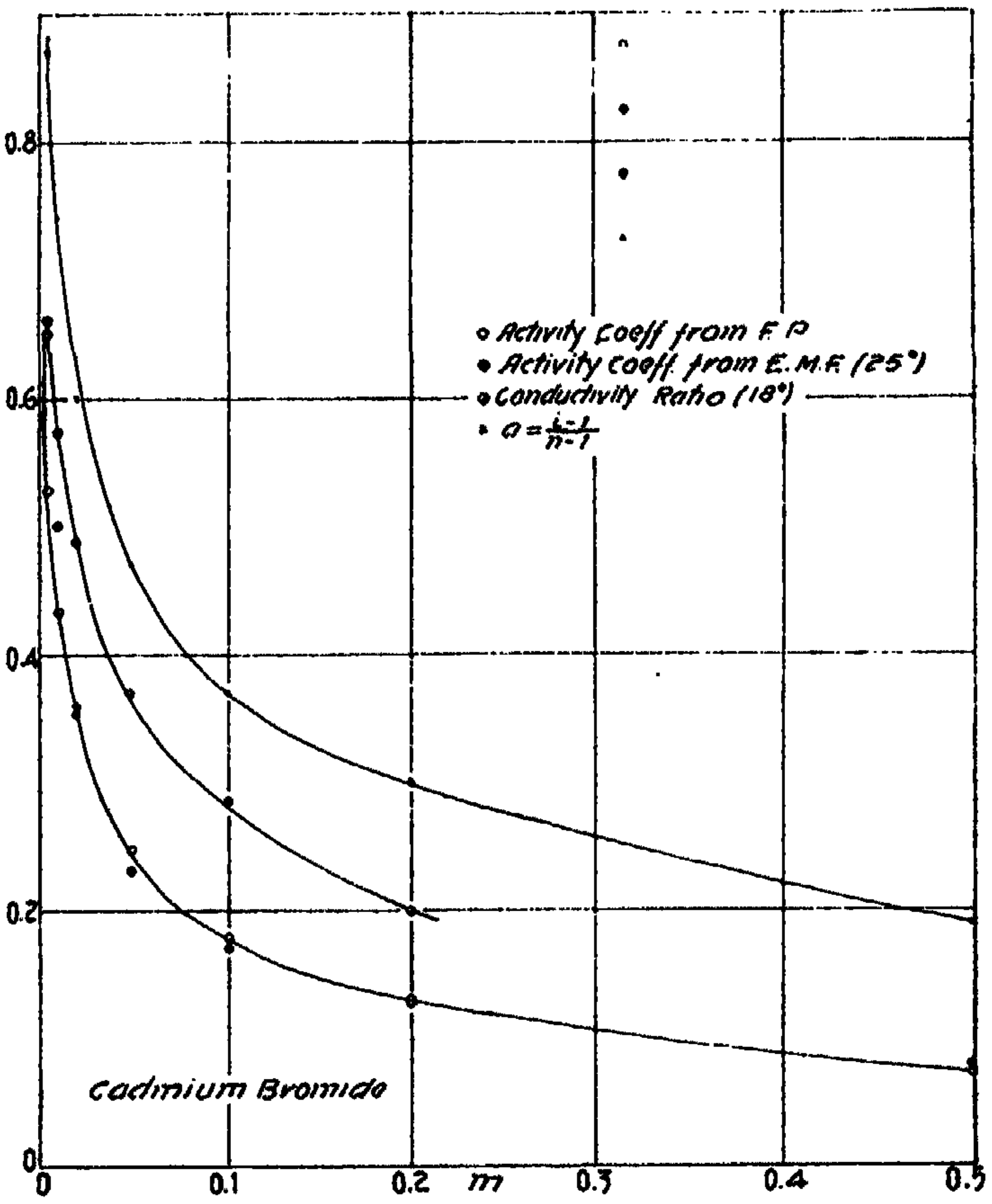

Fig. 4

$$\int_{0}^{0.01} -\, j\, d\log m = -\frac{\beta}{2.303\alpha}(0.01)^{\alpha} \qquad (3)$$

The value of the first integral in equation (1) between infinite dilution and 0.01M can be calculated by equation (3); its value between 0.01M and

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[26] Lewis and Linhart: J. Am. Chem. Soc., 41, 1952 (1919).

higher concentrations can be found by plotting j against log m and measuring the area subtended by the curve between 0.01M and the successive limits by means of a planimeter. In like manner the second integral in equation (1) can be evaluated by plotting θ/m against θ and measuring the corresponding areas under the curve.

Applying equation (1), in the manner outlined, to the data of Tables I to III, the values of γ' given in the sixth column of Tables IV to VI were derived.

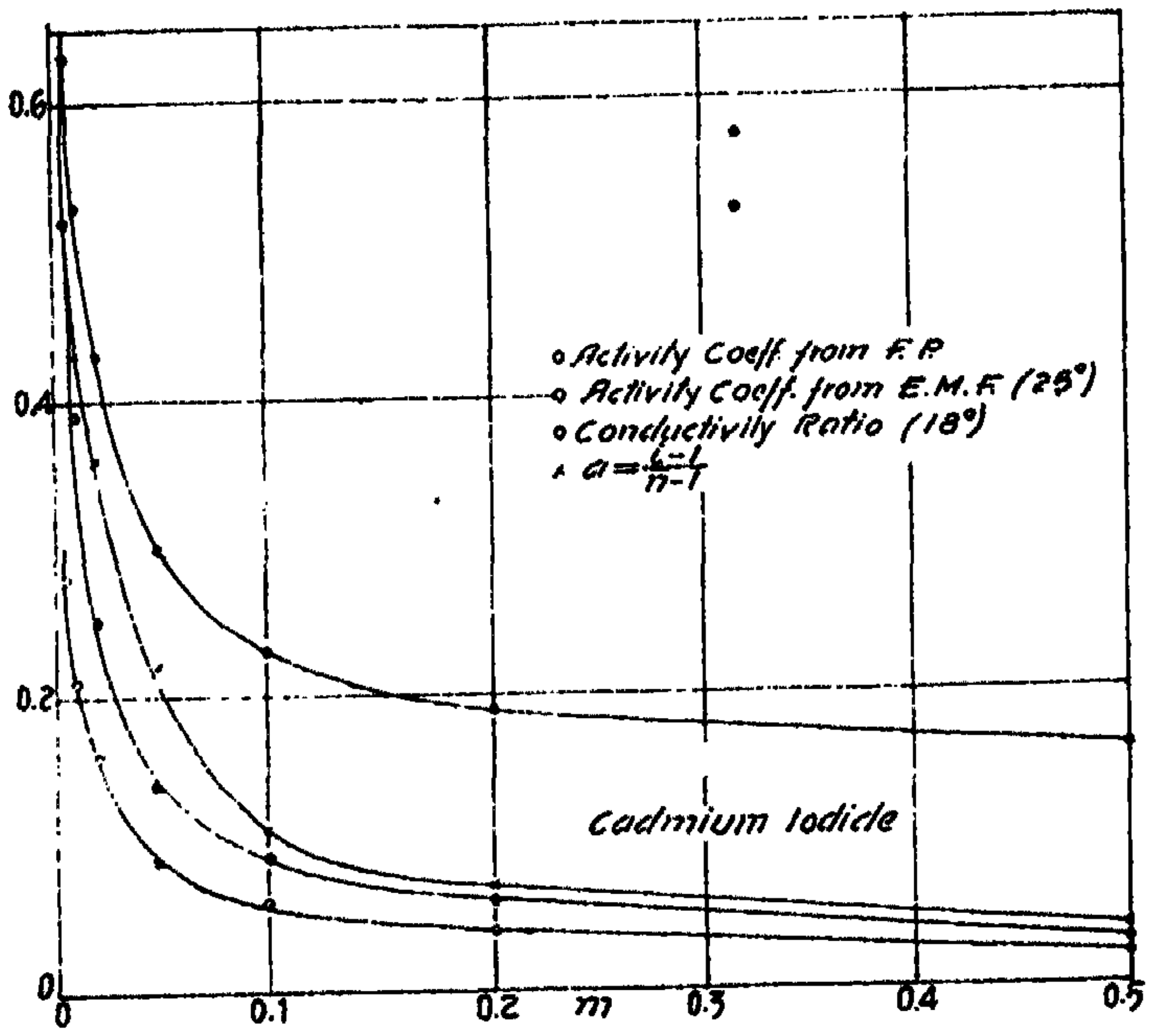

Fig. 5

Table IV

Activity Coefficients of Cadmium Chloride

m	θ/m	i	α(f.p.)	Λ/Λ_0(18°)	γ'	γ(25°)
0.005	——	——	——	0.735	0.648	0.76
0.01	5.1	2.74	0.87	0.664	0.567	0.64
0.02	4.50	2.42	0.71	0.584	0.484	0.49
0.05	3.99	2.15	0.57	0.453	0.380	0.31
0.1	3.66	1.97	0.49	0.375	0.289	0.21
0.2	3.35	1.80	0.40	0.293	0.210	0.15
0.5	2.78	1.50	0.25	0.217	0.130	0.09

For comparison with the values of γ', the values of γ at 25°, as previously derived from our measurements of the electromotive force of cadmium cells (1), are given in the last columns of the tables. The corresponding values of the conductance ratios, Λ/Λ_0, together with values of α as calculated from the freezing point data by the formula, $\alpha = (i - 1)/(n - 1)$ are also included in the tables for comparison. The data of Tables IV to VI are shown graphically in Figs. 3, 4 and 5.

TABLE V

Activity Coefficients of Cadmium Bromide

m	θ/m	i	α(f.p.)	Λ/Δ_0(18°)	γ'	γ(25°)
0.005	——	——	——	0.660	0.527	0.65
0.01	4.60	2.48	0.74	0.572	0.432	0.50
0.02	4.05	2.18	0.59	0.486	0.354	0.36
0.05	3.60	1.94	0.47	0.370	0.249	0.23
0.1	3.24	1.74	0.37	0.286	0.179	0.17
0.2	2.97	1.60	0.30	0.200	0.127	0.12
0.5	2.54	1.37	0.19	——	0.072	0.08

TABLE VI

Activity Coefficients of Cadmium Iodide

m	θ/m	i	α(f.p.)	Λ/Λ_0(18°)	γ'	γ(25°)
0.005	——	——	——	0.63	0.280	0.52
0.01	3.43	1.85	0.43	0.53	0.209	0.39
0.02	3.19	1.72	0.36	0.43	0.159	0.25
0.05	2.70	1.45	0.22	0.30	0.091	0.14
0.1	2.26	1.22	0.11	0.23	0.062	0.09
0.2	2.04	1.10	0.05	0.19	0.037	0.06
0.5	2.02	1.09	0.04	0.16	0.020	0.03

Discussion of Results

Inspection of the foregoing data reveals the fact that the values of γ' and γ for cadmium bromide are in fair agreement throughout the entire range of concentrations studied. This conforms to the results of similar calculations made by Lewis and Randall for sodium and potassium chlorides and sulphuric acid. When we compare the two sets of values of the activity coefficient for cadmium chloride and iodide, however, we discover that they agree only in the more dilute solutions. The values of γ' for the more concentrated solutions of the chloride are found to be greater than the corresponding values of γ, whereas, in the solutions of the iodide the values of γ' are found to be less than the corresponding values of γ. These differences between the values of the activity coefficients, as determined by the freezing point and electromotive force methods, are too great to be explained by the absence of the thermal data required for the correction of the activity coefficients as determined by the former method, for it has been shown by Lewis and Randall[25] that failure to apply the correction for thermal effects to the values of the activity coefficients of solutions of sodium chloride, determined by the freezing point method, produces no appreciable error in the dilute solutions and introduces an error of not more than 3 per cent in the value of γ for a molal solution.

As the result of an extensive comparison of the ionization values of typical electrolytes, derived from freezing point depressions and conductivity ratios, Noyes and Falk[27] pointed out that the two methods give ionization values which, for most univalent substances, agree with each other within 2 per cent up to 0.1M, and that the same is true of the unibivalent salts, potassium sulphate and lead nitrate, even up to 0.2M. The halides and sulphates of bivalent metals, on the other hand, were found to show much larger deviations than this at 0.1M and 0.2M. The halides of cadmium were found to present wide divergence between the two sets of ionization values, the values of α derived from freezing point data being as a rule larger than the corresponding values derived from conductivity data. Commenting on this divergence, Noyes and Falk point out that the transference numbers of these same salts are also abnormal in that the cation transference number decreases markedly with increasing concentration.

The tendency of the cadmium halides to form complex molecules and ions in solution suggests a possible explanation of these divergences. Thus, Schmidt[28] and Bruns[29] have adduced evidence in favor of the existence in solution of not only simple molecules of CdI_2 but also of molecules having the composition Cd_3I_6, which in dilute solution are assumed to ionize according to the scheme:

$$Cd_3I_6 \leftrightarrows Cd^+ + Cd_2I_6^-.$$

In more concentrated solutions even larger aggregates are believed to be present, such as Cd_4I_8, Cd_5I_{10} or in general $(CdI_2)_n$, the last undergoing ionization as follows:

$$(CdI_2)_n \leftrightarrows Cd^+ + Cd_n - I_{2n}.$$

It is equally probable that the chloride and bromide of cadmium behave in like manner when dissolved in water. In his treatment of the halides of the bivalent metals, Ephraim[30] states that, "There is thus every indication that some at least of the salts under consideration have two or three molecules conjoined in the crystal state, *a structure which persists even in the ions.*"

It was pointed out by Jones and his co-workers[31] that the molal depressions of the freezing point of a wide variety of solutes pass through a minimum value as the concentrations of their solutions are increased. The concentration at which this minimum usually occurs was found to be in the neighborhood of 0.2M. In order to account for the existence of this minimum, it was suggested that the dissolved substance undergoes hydration in

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[27] Noyes and Falk: J. Am. Chem. Soc., 34, 485 (1912).

[28] Schmidt: Ann. Physik, (4), 75, 337 (1924).

[29] Bruns: A. physik. Chem., 34, 751 (1925).

[30] Ephraim: "A Text-book of Inorganic Chemistry," translated by P.C.L. Thorne, 221 (1926).

[31] Jones: Carnegie Institution of Washington, Publication No. 60.

solution and thus, as the concentration of the solution is increased, less and less water remains available to function as solvent and a progressive rise in the molal depression of the freezing point occurs. A similar process may reasonably be assumed to take place in solutions of the cadmium halides, especially since it has been shown that those substances which crystallize from their solutions with water of crystallization are almost without exception prone to exhibit marked hydration in solution. In the case of the cadmium halides, however, the presence of a relatively large number of complex solute molecules, with their resultant complex ions, should tend to cause a displacement of the minimum in the direction of increasing concentration. Reference to the curves of molal depression of the freezing point of these salts, shown in Fig. 2, confirms this prediction. Within the range of concentration comprised by these experiments, it is apparent that cadmium iodide is the only one of the three salts whose freezing point curves pass through a minimum.

In view of the various complicating factors involved in the solution and ionization of the cadmium halides, it is, therefore, scarcely to be expected that the values of the activity coefficients of their solutions derived from measurements of freezing point depression, on the one hand, and from measurements of electromotive force, on the other, should be in agreement except in extreme dilutions.

Summary

(1) The freezing points of aqueous solutions of the chloride, bromide, and iodide of cadmium have been measured by means of a platinum resistance thermometer from 0.01M to 0.5M.

(2) From the freezing point data thus obtained, the activity coefficients, uncorrected for thermal effects, have been calculated and compared with corresponding data previously derived from electromotive force measurements.

(3) The lack of agreement between the two sets of values has been discussed and is attributed to the many conflicting factors which are involved in the solution and ionization of the cadmium halides.

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THE DECOMPOSITION OF ACETONE IN CONTACT WITH PLATINUM

BY H. AUSTIN TAYLOR

The comparisons that have so far been made between homogeneous and catalysed reactions are confined to those reactions that are of second order in the gas phase, becoming in general unimolecular when suitably catalysed. The function of the catalyst seems to be to allow a series of simple reactions to occur, the energy of activation of any single step being less than that of the homogeneous reaction. The problem naturally arises: what effect will a catalyst have on a truly homogeneous unimolecular reaction?

In an attempt to solve this problem the reaction chosen was the decomposition of acetone which Hinshelwood and Hutchinson[1] have shown to be truly unimolecular. There appears to be some possible doubt about the actual reaction which was studied in this case, namely whether, as the authors claim, it is the primary split into carbon monoxide and free methyl groups, or whether it is actually the decomposition of ketene. Whatever the true answer may be, suffice that here evidence is given that it is the same reaction being studied in both cases.

That acetone is readily decomposed catalytically has been shown by Sabatier.[2] "The decomposition occurs slowly at 240° and rapidly at 270° in presence of nickel, yielding carbon monoxide and the CH_3 radicals which give a little ethane and ethylene but chiefly methane, hydrogen and carbon." It is the latter substance, carbon, that precludes the use of nickel as a catalyst for kinetic measurements. Several attempts were actually made to follow the reaction in this manner. It was found possible to obtain a single velocity curve with a freshly prepared catalyst[3] but the deposition of an apparently abnormal amount of carbon even at 200° almost complctly poisoned the catalyst for succeeding runs, so the method was discontinued.

The action of platinum sponge and palladium black on ketones is stated by Sabatier to be less intense. It seemed likely therefore that the bulk metal would be somewhat active though perhaps only feebly. This less intense action might reduce the quantity of carbon formed, since Hinshelwood found only a slight blackening of the reaction vessel in the homogeneous decomposition. The poisoning action would consequently also be reduced. The method adopted therefore was to study the decomposition on a hot platinum filament stretched axially across the reaction vessel which was kept at a constant temperature of 50° in a thermostat. The reaction was followed by the pressure change with an apparatus similar to that used by Hinshelwood,

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[1] Proc. Roy. Soc., **111A**, 245 (1926).

[2] Ann. Chim. Phys., (8) **4**, 474 (1905).

[3] The catalyst was nickel reduced from the nitrate supported on pumice.

the manometer and capillary connecting tube being wound with fine nichrome wire and maintained as near to 50° as practicable to maintain the acetone gaseous during a run.

Acetone, purified by the standard bisulphite method and then twice distilled, was finally distilled into a small flask sealed to the reaction vessel through a three-way stopcock. The apparatus was evacuated by means of an oil pump for at least thirty minutes between runs, the filament being allowed to glow during the latter part of the evacuation. This was found necessary to avoid the slight induction period which is apparent in some of the results at the low temperature, and may have been due to adsorbed hydrocarbons or possibly carbon itself on the filament. In order to maintain the temperature of the filament constant throughout a run, and avoid temperature changes due to the changing thermal conductance of the surroundings, its resistance was kept constant by placing it in one arm of a Wheatstone Bridge, the standard resistance being of 3 ohms and capable of carrying 15 amps. The current actually consumed being only about 1.5 amps. the heating effect in the latter, and consequently the change in resistance was negligible. The 'bridge' itself consisted of two 10,000 ohm variable resistance

TABLE I

A. Temperature = 844°C			
Initial Pressure	t_{25}	t_{50}	t_{75} mins.
393	7.0	18.4	59.0
315	7.4	17.4	47.6
302	6.8	16.6	43.2
253	6.4	15.2	32.4
252	7.0	17.0	37.4
237	6.9	17.2	36.4
226	8.6	21.6	53.0
165	8.6	22.0	54.0
B. Temperature = 890°C			
382	2.4	7.2	27.0
331	2.4	6.0	17.5
273	2.4	6.0	15.0
268	2.1	5.4	12.7
229.5	2.2	5.5	12.6
182.5	1.9	4.6	9.8
C. Temperature = 916°C			
413	1.1	3.5	17.0
360	1.1	3.1	15.0
303.5	1.1	2.9	8.7
237.5	1.15	2.4	6.0
173	0.8	2.3	6.2

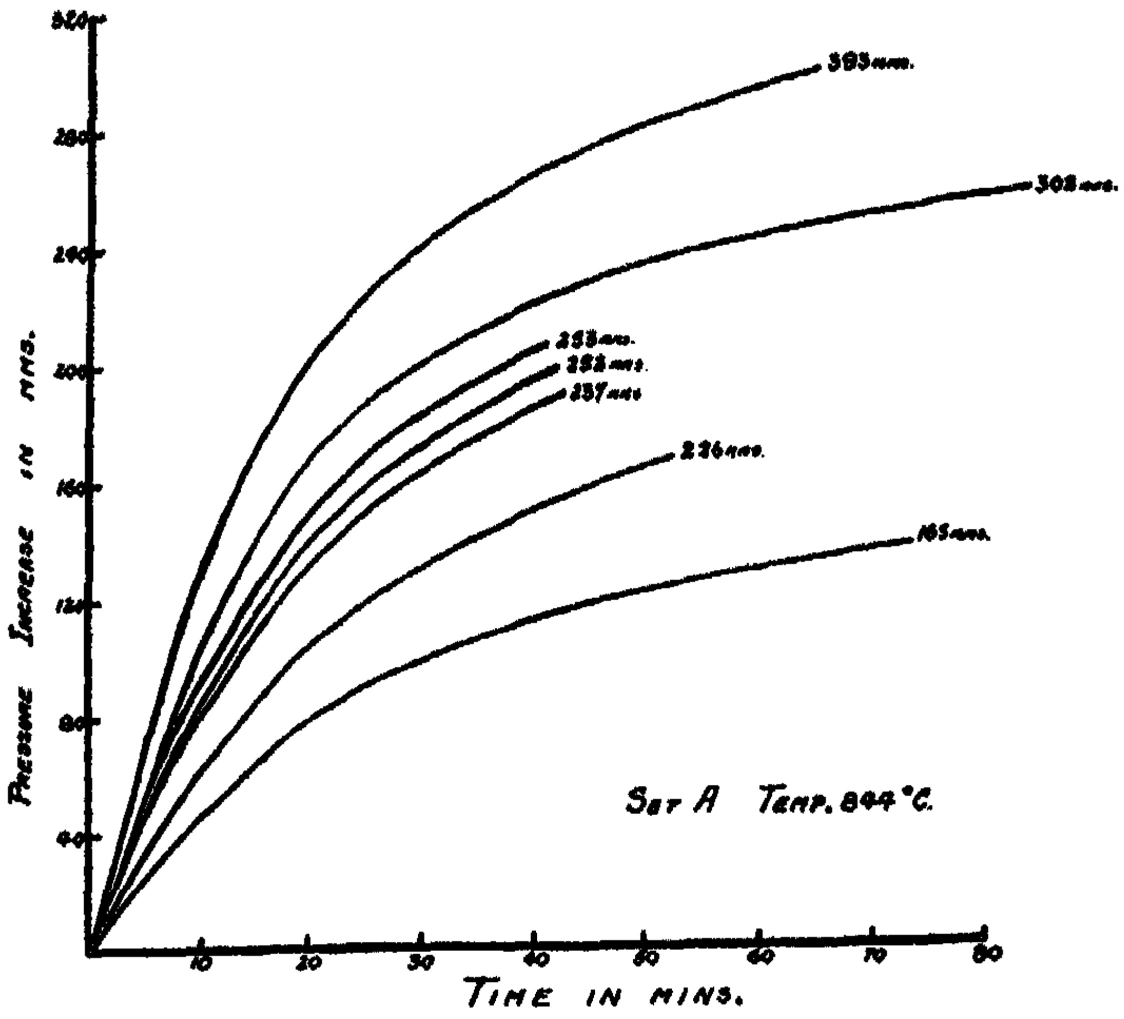
320
280
240
200
160
120
80
40
Pressure Increase in mms.
393 mm.
302 mm.
253 mm.
252 mm.
237 mm.
226 mm.
165 mm.
Set A Temp. 844 °C.
10
20
30
40
50
60
70
80
Time in mins.

Fig. 1

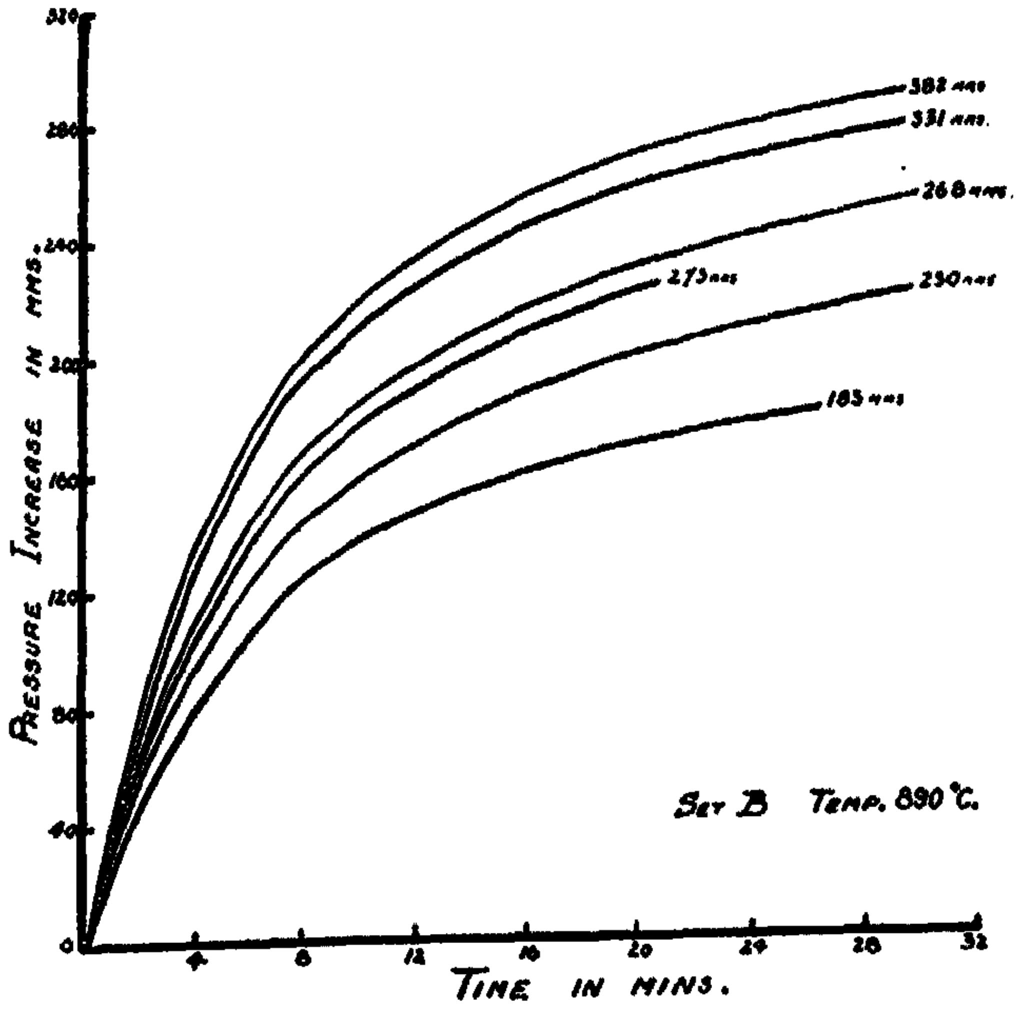
320
280
240
200
160
120
80
40
0
Pressure Increase in mms.
382 mm.
331 mm.
268 mm.
273 mm.
230 mm.
183 mm.
Set B Temp. 890 °C.
4
8
12
16
20
24
28
32
Time in mins.

Fig. 2

boxes so that the current carried by them was also negligible. A delicate galvanometer was used for the balance, which was maintained by varying the external current through a rheostat. That some such arrangement was necessary is shown by the fact that the current consumed during runs varied by 0.2 amp. between the beginning and end. The actual temperature of the filament was obtained with an optical pyrometer, an auxiliary object lens being used the better to focus the filament. These temperatures were checked by the resistance of the filament, a small correction due to the cold ends being necessary.

Measurements were made at three different temperatures using varying initial pressures of acetone. The somewhat surprising result was that in all cases the course of the reaction was quite similar to that found by Hinshelwood and susceptible to the same analytical treatment. The degree of concordance between successive runs does not appear to be quite so good as in the homogeneous reaction, which may probably be accounted for by the changing catalytic effect on one or other of the reactions occurring.

That the reaction is unimolecular may be judged from Table I which gives the times taken for the initial pressure to increase by 25, 50 and 75 per cent.

The results of t_{25} and t_{50} are ample evidence that the reaction is essentially unimolecular. The variations in the values of t_{75} are no doubt due to the subsequent reactions that are possible after the initial decomposition has occurred. That such reactions when taken into consideration would better the agreement between the various values at t_{25} and at t_{50} as well, can be seen in the following examples of t_{25} corrected for B in Table I. The values become 1.5, 1.6, 1.6, 1.6, 1.6, 1.5 respectively.[1] There can be no doubt therefore as to the order of the reaction in general. The results obtained for the rate of pressure increase with time are shown in the following diagrams, one for each temperature as stated.

The curves are identical in form with those in the homogeneous reaction being unimolecular in character up to approximately 70 per cent of the change but from that point on continuing to increase slowly but steadily, instead of reaching a maximum value. Hinshelwood has suggested this to be due to the subsequent reactions of the free methyl groups, in which case the limiting slope of the observed curve would correspond to the pressure increase accompanying those reactions. By extrapolating back to zero time as in Fig. 4, the value of the pressure increase is obtained that would have been observed had the primary decomposition of the acetone alone occurred. This value is the value to which the pressure increase becomes asymptotic for the simple unimolecular decomposition. The observed pressure increases after different time intervals are therefore greater by an amount which is the difference between the above asymptotic value and the limiting slope of the

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[1] The value 2.2 above must not be compared with the 1.6 here given since the former is the time taken for the initial pressure to increase by 25 per cent., whereas the latter is calculated on the basis of the primary decomposition alone, as shown later.

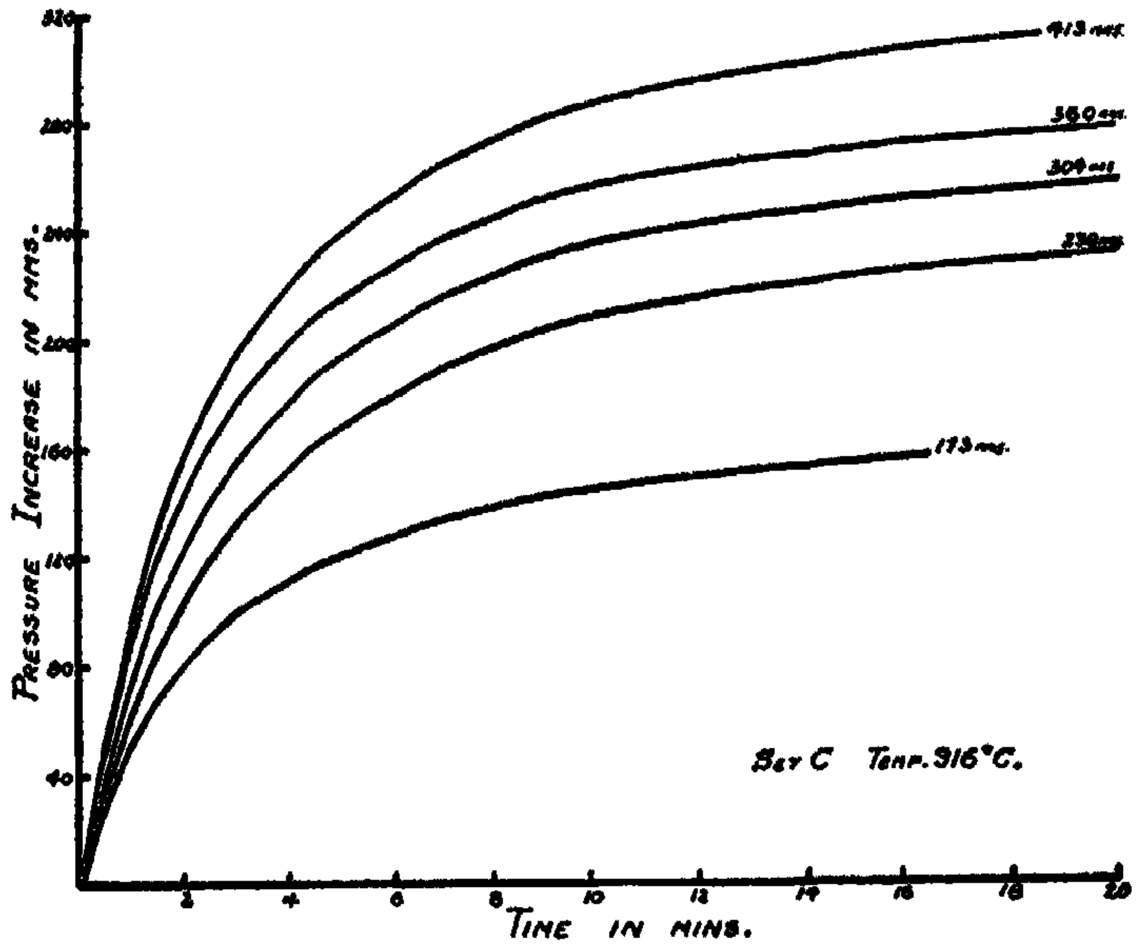
Pressure Increase in mms.
320
280
240
200
160
120
80
40
Time in mins.
2
4
6
8
10
12
14
16
18
20
413 mm.
360 mm.
304 mm.
238 mm.
173 mm.
Set C Temp. 316°C.

Fig. 3

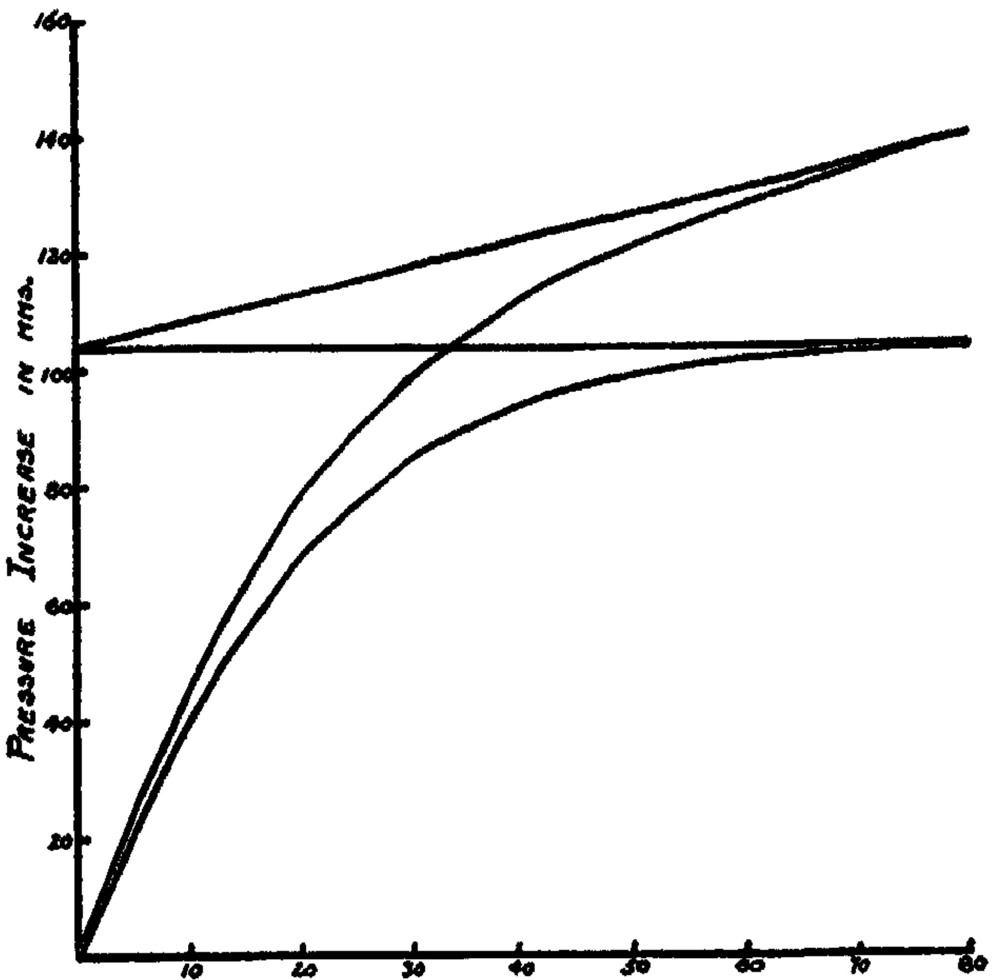
Pressure Increase in mms.
160
140
120
100
80
60
40
20
Time in mins.
10
20
30
40
50
60
70
80

Fig. 4

observed curve at each particular time. It is therefore a simple matter to construct the ideal unimolecular curve in each case, the lower curve in Fig. 4 being one example.

TABLE II

Time in mins.	Obs. pressure increase in mms.	Corr. pressure increase x	$k = \frac{2.303}{t} \log \frac{104}{104-x}$
0	0	0	—
4	21	18	.0475
8	39	38	.0566
12	54	49	.0531
16	67	60	.0538
20	78	69	.0545
24	87	76	.0547
28	96	82	.0554
32	102	87	.0566
36	107	91	.0578
40	112	94	.0586
44	117	96	.0583
48	120	98	.0594
52	122	99	.0584
56	125	100	.0582
60	128	101	.0591
64	131	102	.0618
68	134	103	.0683
			Mean = .057

TABLE III

A. Temperature = 844° C.

Initial Pressure	Corrected Final Pressure	Mean k
302	220	0.063
165	104	0.057

B. Temperature = 890°C.

Initial Pressure	Corrected Final Pressure	Mean k
382	230	0.208
331	218	0.202
268	192	0.196
273	180	0.208
229.5	162	0.197
182.5	136	0.228

C. Temperature = 916°C.

Initial Pressure	Corrected Final Pressure	Mean k
413	270	0.392
360	246	0.376
303.5	214	0.402
237.5	194	0.358
173	130	0.392

From the values so obtained graphically it is easy to calculate the unimolecular constant at each temperature. Table II gives the results obtained in one case. The initial pressure was 165 mms. and the temperature 844°C. The extrapolated value of the pressure increase is 104 mms. and the unimolecular constant is calculated on that basis as shown.

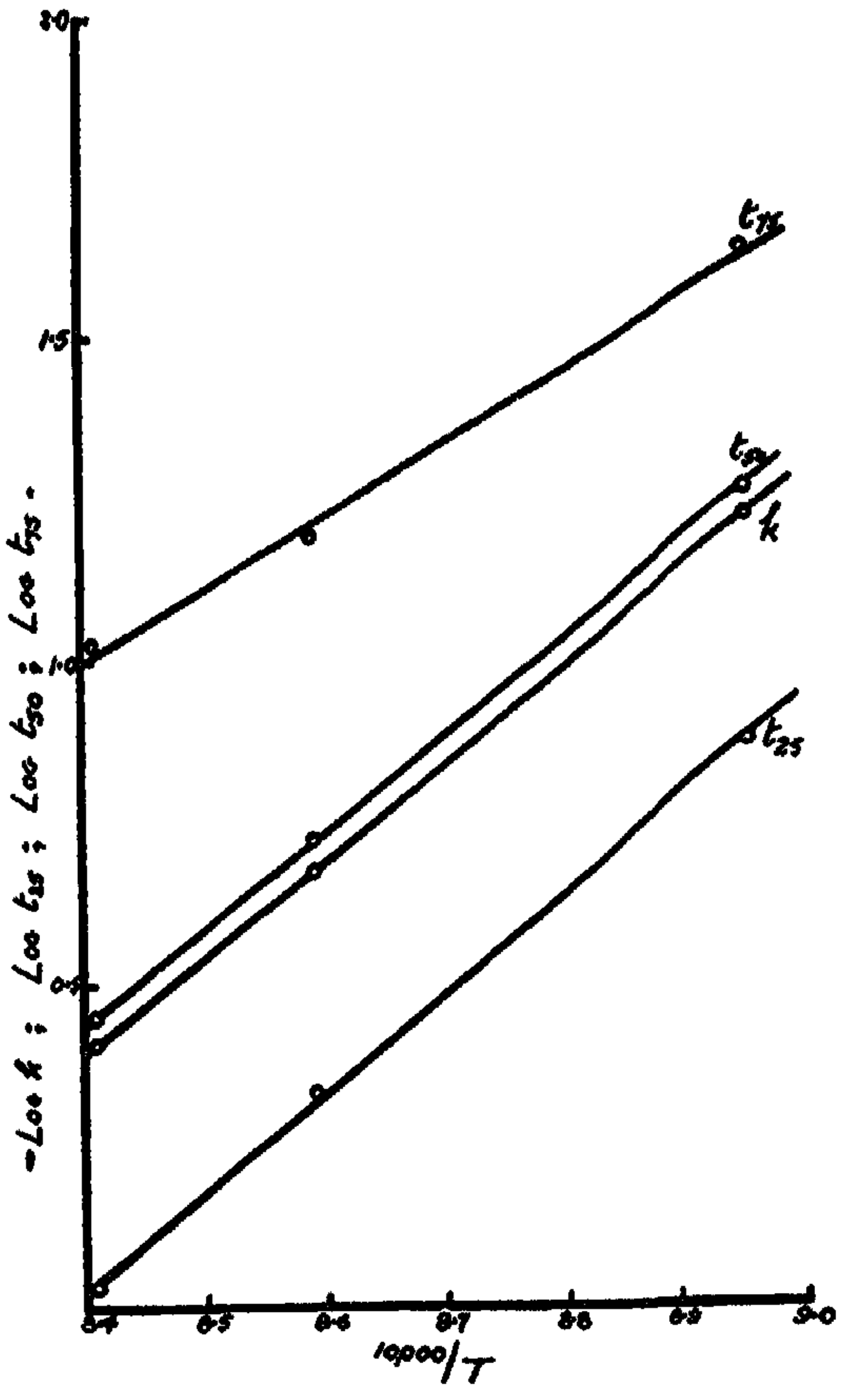

Fig. 5

The degree of constancy is quite good when consideration is taken of the fact that a small error in the limiting slope of the observed curve reflects itself considerably in the constants calculated. Table III summarizes the average constants calculated for various runs made.

That the reaction so studied, and giving the above velocity constants is substantially the same as that observed by Hinshelwood, is evident from the fact that the percentage increase in pressure (corrected) in both cases is of the same order. Hinshelwood cites two cases showing percentage increases of 77 and 79 respectively at different temperatures. The variations here noted are greater than this but show no definite trend either with change of pressure at a particular temperature or with change of temperature. The average increases for example are 75, 68 and 72 percent in sets A, B and C respectively. It seems reasonable to assume then that the corrected pressure increases are due to the same decomposition as in the homogeneous study.

This is further borne out by the calculation of the heat of activation from the velocity constants at the three temperatures. Plotting the logarithms of the velocity constants against the reciprocals of the absolute temperatures the straight line in Fig. 5 is obtained. The slope of this line corresponds to 68,400 calories which is also the average of the values calculated by the Arrhenius equation for the temperature intervals 844-890, 890-916 and 844-916°C. This value is an excellent confirmation of the value 68,500 calories given by Hinshelwood. That the value is not a fictitious one introduced by the particular method of mathematical analysis of the observed results is shown by the accompanying plots on the same figure which are the logarithms of the average values of the previously mentioned times for 25, 50 and 75 per cent increases of the initial pressure (and therefore uncorrected) plotted against the reciprocals of the absolute temperature. The t_{25} and t_{50} values obviously lie on a straight line whose slope is almost identical with that for the velocity constants. The values for t_{75} show a variation which in view of the foregoing is to be expected.

The general conclusion to be drawn from the results therefore would appear to be that the primary decomposition takes place in the gaseous phase in the hot zone immediately surrounding the platinum filament, the latter merely serving as a source of heat and in no way acting catalytically. That the platinum may affect the succeeding reactions is possible. The particular method of analysis would not permit a definite decision on the point although certain irregularities in the later part of the reaction might be taken to suggest a small disturbing effect in the reactions of the methyl groups when compared with the homogeneous case. The observation by Langmuir[1] that carbon monoxide is held to platinum excessively strongly may account in part for the small catalytic effect, in that the surface is practically completely poisoned. It could not however preclude the possibility of activation of a molecule in the immediate neighborhood of the wire by radiation or by actual collision with the poisoned filament. It would seem peculiar that a spontaneous decomposition of the acetone molecule should occur in preference to a bimolecular reaction such as that found by Allen and Hinshelwood[2] in the case of acetaldehyde. The facts presented however prove quite definitely the unimolecular nature of the reaction under all the conditions studied and the identity of the heat of activation herein found, with that for the homogeneous reaction is strong evidence for an identical mechanism.

In so far therefore as the original intention of the paper is concerned, to investigate the catalytic decomposition as compared with the homo-

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[1] Trans. Faraday Soc., **17**, 621 (1922).

[2] Proc. Roy. Soc., **121A**, 141 (1928).

geneous, the work has failed. The point mentioned in an earlier portion however seems worth emphasizing at this stage namely that under other conditions, as for example with an active nickel catalyst, the deposition of carbon is far in excess of that observed during the above work. This would suggest that under the latter conditions the actual decomposition is different from that presumed above. Such a difference might be solely in the subsequent reactions of the methyl group although the possibility exists that the initial decomposition might vary in the two cases as well. It would appear possible then, that under those conditions where a catalytic effect is to be observed the results would not be directly comparable with those for the homogeneous reaction and so the initial object of the work defeated. A decision on the point would require further investigation.

Summary

1. The decomposition of acetone was studied at various temperatures and pressures in contact with a heated platinum filament.

2. The results are identical in form with those for the homogeneous reaction, the same method of mathematical analysis being applicable.

3. The primary decomposition is unimolecular, with an energy of activation of 68,400 calories as compared with 68,500 calories for the homogeneous case, suggesting a homogeneous reaction in a zone around the hot filament, the latter showing no catalytic effect.

4. The large amount of carbon deposited during the decomposition on active nickel presents the possibility of a different mechanism which may not be comparable with the homogeneous change.

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A NEW METHOD FOR EXTRAPOLATING SPECIFIC HEAT CURVES OF ORGANIC COMPOUNDS BELOW THE TEMPERATURES OF LIQUID AIR

BY KENNETH K. KELLEY, GEORGE S. PARKS AND HUGH M. HUFFMAN

Specific heat data on a large number of organic compounds down to the temperatures of liquid air are to be found in the literature. Such data are very useful, for from them the entropies of the substances may be obtained and these together with the heats of combustion enable one to calculate the free energies of formation. The entropy of a substance is obtained by utilizing the equation, $S_T = \int_0^T C_p dT/T$, which means that the heat capacity curves must be extrapolated to 0° K. There has been no satisfactory method suggested heretofore for making this extrapolation. The specific heats at liquid air temperatures are, of course, very much too high for the use of the Debye function alone. A combination of Debye and Einstein functions might be used by empirically fitting each specific heat curve. Such a process would be rather laborious and it is questionable whether or not it would give sufficient accuracy in view of the fact that in the case of organic compounds all heat capacity curves are just entering the range where dC_p/dT is large. The "n" formula method suggested by Lewis and Gibson[1] for simple inorganic substances has been shown to give results 15 to 35% too high when applied to organic compounds.[2]

The method which is suggested here has three advantages, (1) it is based on experimental data down to or below 20° K. and in no way conflicts with any theoretical considerations, (2) it is simple and very easy to apply and (3) it gives sufficient accuracy for most purposes.

Satisfactory specific heat measurements down to or below 20° K have been made on the following substances in the crystalline state—methyl alcohol, ethyl alcohol, hexyl alcohol, isopropyl alcohol, acetone, cyclohexanol, glycerine, glucose, toluene, m-xylene (preliminary), quinone and hydroquinol.[3] The molecular heat capacity curves for these substances fall naturally into two classes—one for aliphatic and one for cyclic compounds. In each class the experimental curves are so similar in character that a typical or standard curve may be easily constructed such that any substance of this class will have at any temperature, approximately, the heat capacity of the standard substance at that temperature multiplied by a factor, this factor being dif-

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[1] Lewis and Gibson: J. Am. Chem. Soc., **39**, 2565 (1917).

[2] See Refs. 3 (a), 3 (b) and 3 (c).

[3] (a) Methyl alcohol, Kelley: J. Am. Chem. Soc., **51**, 180 (1929); (b) Ethyl and Hexyl alcohols, Kelley: **51**, 779 (1929); (c) Isopropyl alcohol and acetone, Kelley: **51**, 1145 (1929); (d) Cyclohexanol, Kelley: **51**, 1400 (1929); (e) Glycerine, Giauque: **45**, 93 (1923); Simon and Lange: Z. Physik **38**, 227 (1926); (f) Glucose, Simon: Ann. Physik, (4), **68**, 258 (1922); (g) Toluene and m-Xylene, Kelley: J. Am. Chem. Soc., **51**, 2738 (1929); (h) Quinone and Hydroquinol, Lange: Z. physik. Chem., **110**, 350 (1924).

ferent for different substances but having the same value at all temperatures below those of liquid air for any one substance. A still better agreement is obtained if a second constant is introduced and we write

$$C_p \text{ (per mole)} = (A + BT)\, C_p^\circ \qquad (1)$$

where C_p° is the molal specific heat of the standard substance.

It has been the custom in the case of most of the experimental work which has been published to extrapolate below 90° K, since this temperature is easily obtained with liquid air. Using equation (1), we find

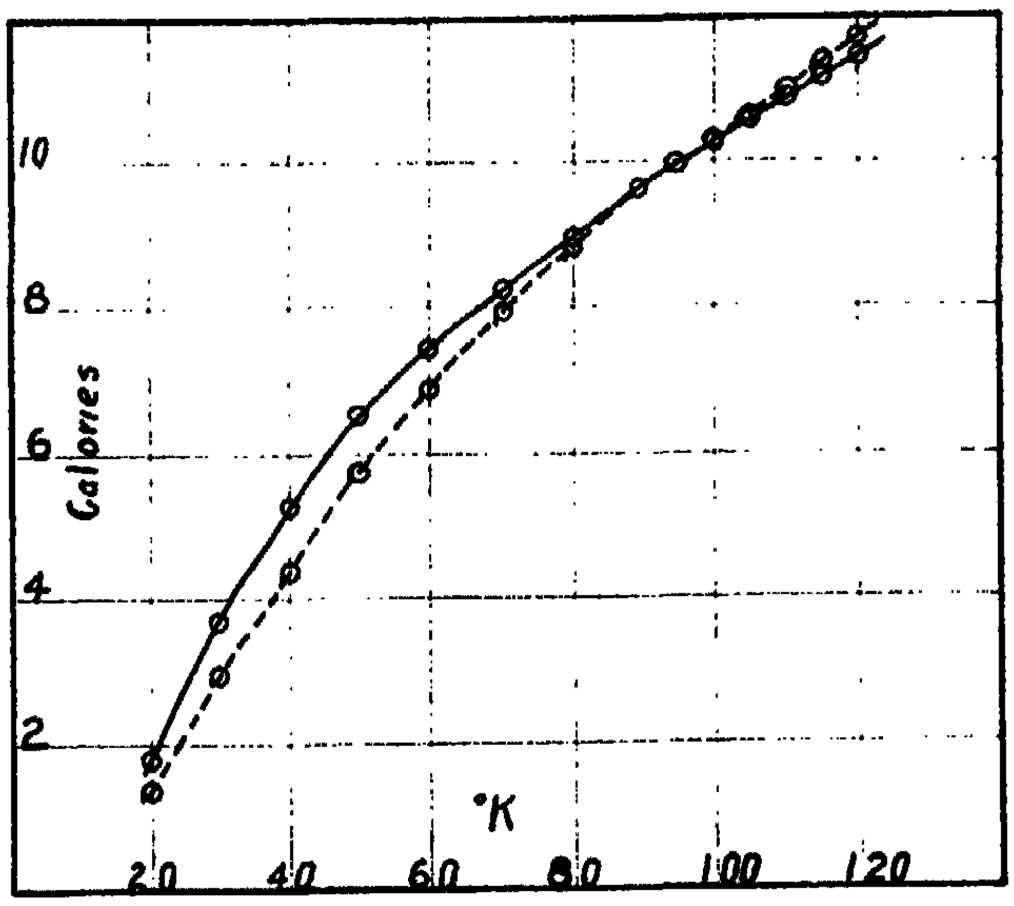

Fig. 1

The broken line gives the molal heat capacity of the standard aliphatic substance. The heavy line is for two-thirds the molal heat capacity of the standard cyclic substance.

$$S_{90} = \int_0^{90} \frac{C_p dT}{T} = A\int_0^{90} \frac{C_p^\circ dT}{T} + B\int_0^{90} C_p^\circ dT = AS_{90}^\circ + B\int_0^{90} C_p^\circ dT, \quad (2)$$

where S_{90} is the entropy of the particular substance we are considering at 90° K and S°_{90} is the entropy of the standard substance at 90°K.

In Table I are given the values of C_p° at various temperatures for the standard substances of each class. These values are plotted against the temperature in Fig. 1, 2/3 C_p° being plotted in the case of the standard for the cyclic class to bring the curves closer together to facilitate comparison.

For any particular substance the values of A and B in equation (1) may now be readily obtained. All that is needed are the molal heat capacities of the given compound at two temperatures, say for convenience 90° and 120°K. These values together with the values for C_p° and the temperature are placed in equation (1) and the two resulting equations solved for A and B.

S_{90}° and $\int_0^{90} C_p^{\circ}dT$ were obtained by graphical integration, extrapolation below 20°K. being made by means of Debye functions. This latter part is small and therefore no appreciable errors in the values of S°_{90} and $\int_0^{90} C_p^{\circ}\,dT$ result. At the bottom of Table I are given the values of these two quantities for both standards.

TABLE I

Data for Standards (per mole)

Temp., °K.	Class I Aliphatic Compounds C°_p cal.	Class II Cyclic Compounds C°_p cal.	Temp., °K.	Class I Aliphatic Compounds C°_p cal.	Class II Cyclic Compounds C°_p cal.
20	1.38	2.65	95	9.98	14.67
30	2.87	5.45	100	10.30	15.15
40	4.40	7.80	105	10.65	15.61
50	5.75	9.65	110	11.00	16.05
60	6.92	11.00	115	11.34	16.50
70	7.95	12.15	120	11.70	16.90
80	8.84	13.22	S_{90}°	8.05E.U.	13.7 E. U.
90	9.64	14.20	$\int_0^{90} C_p^{\circ}dT$	432 cal.	697 cal.

In Table II are compared the values of S_{90} obtained by this method of extrapolation with the values of S_{90} obtained directly from the experimental measurements for the twelve substances listed above. In no case is the difference greater than 0.6 E. U. or than 5.7% of the experimental values of S_{90}. The average difference is 0.3 E. U. or about 2.6%.

TABLE II

Molal Entropy Values for Twelve Compounds at 90°K.

Substance	S_{90} (measured)	S_{90} (calculated)	Difference
Methyl Alcohol	7.9 E. U.	8.3 E. U.	+0.4E. U.
Ethyl Alcohol	9.5	9.0	−0.5
n-Hexyl Alcohol	14.0	14.6	+0.6
iso Propyl Alcohol	10.6	10.0	−0.6
Acetone	12.9	12.4	−0.5
Glycerine	9.9	10.1	+0.2
Glucose	13.2	13.3	+0.1
Toluene	14.5	14.6	+0.1
m-Xylene	15.9	16.0	+0.1
Quinone	13.5	13.2	−0.3
Hydroquinol	10.4	10.5	+0.1
Cyclohexanol	11.6	11.4	−0.2

This method has been applied recently by the authors[1] in the revision of the entropies and free energies of nineteen of the organic compounds for which there were experimental specific heats down to 90°K. In no case was there any reason to believe that a satisfactory extrapolation had not been obtained.

Summary

A new method for extrapolating heat capacity curves of organic substances below the temperatures of liquid air for the purpose of obtaining the entropies has been suggested.

Department of Chemistry,
Stanford University, Calif.
May 1, 1929.

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[1] Parks, Kelley and Huffman: J. Am. Chem. Soc., **51**, 1969 (1929).

THE HYDRATION OF SUCROSE IN AQUEOUS SOLUTION

BY JAMES W. McBAIN AND S. S. KISTLER

Proof of the existence or non-existence of hydrates in solution is of considerable importance to an understanding of solution phenomena. However, even the simpler solutions, such as those of sucrose in water, which are not complicated by ionization phenomena, have not given themselves readily to a direct determination of the degree of hydration, and numerous indirect methods of inference of more or less doubtful value have had to be relied upon.

Phillip[1] calculated from Steiner's[2] results on the solubility of hydrogen in aqueous sucrose solutions the degree of hydration of the sucrose molecules with the following results:

Percentage sugar	16.67	30.08	47.65
Mols. water per mol. sugar	6.5	6.0	5.4

H. C. Jones[3] and collaborators determined the degree of hydration by observing the broadening of the absorption bands of cobalt salts with concentration of the solution. E. W. Washburn[4] evaluated the freezing-point data for sucrose solutions from Loomis, Morse and Frazer, Raoult, and Ewan and found that up to a 2 molar solution the degree of hydration is 6. By applying his equation for the viscosity of colloidal solutions to 1.0% sucrose in water, Einstein[5] calculated that there are seven molecules of water attached to each molecule of sugar. The calculation involves the assumption that the molecules of sugar are very large spheres compared to the molecules of water. Scatchard[6] finds evidence of a hexahydrate from osmotic pressure measurements. Miss F. M. Hunter[7] assumes that hydration accounts for deviations of the osmotic data of Morse[8] and similarly calculated data from the heats of dilution applied to Morse's data for 20°. Using the equation $(P(v-b) = RT$, and taking the hydration as the excess of b over the volume of solid sucrose, 0.214 liter (Einstein uses 0.209), the following values were obtained:

Molality of sugar	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Hydration deduced from deviation from perfect gas law.	44	16	11	8	7	6	6	6	6	6

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[1] Trans. Faraday Soc., 3, 141 (1907).

[2] Wied. Ann., 52, 275 (1894).

[3] H. C. Jones: "Hydrates in Aqueous Solutions," Carnegie Inst. Washington (1907).

[4] Mass. Inst. Tech. Quarterly, 21, 377 (1908).

[5] Ann. Physik, 4, 34 (1911).

[6] J. Am. Chem. Soc., 43, 2387 (1921).

[7] Trans. Faraday Soc., 22, 1194 (1926).

[8] Am. Chem. J., 48, 29 (1912).

It is to be noted that Einstein's calculation of seven was for a 0.03 M solution. McBain takes this incompatibility to indicate that Morse's data for dilute solutions are wrong, or rather that residual error in dilute solutions is unduly magnified by such calculations.

By using the method of ultrafiltration first used by McBain and Jenkins[1] in the determination of the degree of hydration of soaps in solution, we have been able to make the first direct measurements of the hydration of sucrose.

Materials and Apparatus

The ultrafilter used was of bronze, manufactured by the Vereinigung Göttinger Werke. In order to avoid any possibility of reaction with the bronze, the inside of the filter was heavily silver plated, and all parts that would come in contact with the solution were either made of silver or heavily silver plated. Nickel gauze, 200 mesh, was used under the membrane.

The membranes used were of the type developed by McBain and Kistler.[2] Number 600 cellophane (duPont) was soaked in water for a short time and then transferred to 95% ethyl alcohol and allowed to stand for from fifteen minutes to half an hour. It was then placed in the ultrafilter and a small quantity of "Parlodion" (duPont) nitrocotton dissolved in 10 ml. of 50-50 alcohol-ether filtered through at a pressure of 50 atmospheres. The quantity of nitrocotton was sufficient to form a film over the surface of the cellophane of 0.0005-0.0001 cm. thickness. The ability of the membrane thus formed to filter sucrose out of solution was found to be largely dependent on the concentration of the water in the alcohol-ether solvent. By using absolute alcohol and ether, very thin membranes proved to be good molecular sieves. The thin membranes are very tender, however, and soon deteriorate, probably because of the formation of bubbles of nitrogen under and in them when the pressure is released, so that we found that thicker membranes, deposited from solvent containing approximately 10% water, were more satisfactory. One such membrane removed over 90% of the sugar from a 35% solution with a satisfactory rate of filtration and continued in good condition for eight days before showing signs of disintegration, in spite of frequent changes of pressure of 75-100 atmospheres. One membrane was made by filtering a small quantity of viscose solution diluted in water through a No. 600 membrane previously soaked in water. The viscose had been kept on ice since it was made so that no ripening or ageing had occurred. This membrane retained approximately 60% of the sugar from a 33% solution.

The sugar used for the first part of the work was commercial cane sugar, dried at 60°. For the last half of the work C.P. saccharose (Merck) was used. No sensible difference in the sugar obtained from the two sources was noted. The specific rotations of the two samples were within 0.05% of each other. The methyl alcohol used was Baker's Special C.P. Absolute. Pressures were obtained by connecting to a cylinder of nitrogen.

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[1] J. Chem. Soc., 121, 2325 (1922).

[2] J. Gen. Physiol., 12, 187 (1928).

Experimental Procedure

Our work rests upon the following principle: if a solution of sugar in water containing a little of some reference substance, in this case methyl alcohol, of such small molecular volume that its concentration is unaffected by filtration, is forced through a membrane of sufficient fineness to hold back some or all of the sugar, there will be a concentration of the reference substance in the filtrate and a corresponding dilution in the residual unfiltered solution in case the sugar molecules retain combined water not available as solvent.

A preliminary investigation revealed that suitable reference substances are scarce when the membranes have sufficiently fine structure to hold back the major part of dissolved sucrose. Salts of the alkali metals were somewhat concentrated by filtration. Methyl alcohol has proved satisfactory in that its aqueous solutions filter in nearly unchanged proportion, particularly since we developed an analytical method that enables its rapid and accurate determination in small quantities.

After forming the membrane *in situ*, water is forced through it to remove the ethyl alcohol and ether. Methyl alcohol solution of the strength to be used later with the sugar is then forced through till the filtrate and residue are of the same concentration. In order to facilitate arrival at this condition, it is expedient to add some alcohol solution and force part of it through, drain the filter and repeat the process until analysis shows satisfactory concentrations. With some of the membranes used, there was evidence that part of the methyl alcohol was being held back, so that it was usually considered satisfactory if the solutions above and below the membrane checked within 1%. The ultrafilter is then rinsed out with some of the sugar-methyl alcohol-water solution that is to be used in the experiment, and the charge added and placed under pressure. In the later experiments we used charges of approximately 100 ml. It is needless to say that the pressure must be higher than the difference between the osmotic pressures of the residue and filtrate. Practically, pressures between 50 and 100 atmospheres have been found advisable. Usually at the same time that the filtrate was collected for analysis, we relieved the pressure and sampled the residue in the filter. That enabled us very nicely to follow the course of the changes occurring.

Analysis is carried out as follows. A carefully calibrated polarimeter tube is weighed and the whole or a part of the sample to be analyzed added and weighed. If all of the sample is used, it enables a better check of the degree of accuracy than if only a part is taken. The tube is then filled with water, closed, and the contents thoroughly mixed by standing first on one end and then on the other till the average density is uniform from one end to the other. It is then grasped by the middle and rotated rapidly about an axis normal to it until it is optically homogeneous. The whole process usually involves about five minutes. This procedure was selected, rather than diluting the sample in a graduated flask and filling the polarimeter tube with an aliquot part, in the interest of accuracy. After the optical rotation is measured and the temperature taken, the solution is discharged into a small distilling flask, the tube rinsed out with distilled water, and the rinsings also added to the flask. From one half to two thirds of the solution is distilled, condensing in a condenser with an internal diameter of 4-5 mm. The distillate is diluted to a definite volume, and aliquot parts taken for analysis for alcohol.

In the earlier work the methyl alcohol was determined by obtaining the density of the distillate with a pyknometer. Where the original sample was only between 5 and 10 ml. and contained only 1 or 2 per cent alcohol, it was found impossible to obtain the requisite accuracy with a pyknometer, and it became imperative to find some other analytical method. Our later procedure was to add the sample of the distillate to a small Erlenmeyer flask containing an excess of sodium dichromate dissolved in sufficiently strong sulfuric acid to make the final strength not less than 12 N. The flask is corked loosely and heated for ten minutes on a water bath. Under these conditions the alcohol is oxidized rapidly and completely to carbon dioxide and water. The solution is transferred to an electrometric titration apparatus and the excess dichromate titrated with ferrous sulfate. The electrometric determination of the end-point is beautifully simple and is one of the most accurate determinations in quantitative analysis.[1]

The accuracies obtainable in these analyses are satisfactory, being within 0.3% or less for the sucrose and 0.2% for the methyl alcohol.

Calculations

It is not practical to make the membranes so dense that no sugar will pass through, since the time required for filtering would be inordinately long and it would be very difficult, if not impossible, to find a reference substance that would not likewise be concentrated to a very troublesome extent above the membrane. Hence the effect of partial transmission of the sucrose must be allowed for by calculation.

By assuming that only water and not alcohol is attached to the sucrose molecule, one can readily calculate the degree of hydration from the concentrations of the sucrose and alcohol above and below the membrane. Let Ms_1 and Ma_1 represent the molalities of the sugar and alcohol, respectively, above the membrane, and Ms_2 and Ma_2 the corresponding molalities below the membrane. Call the number of water molecules attached to a sugar molecule X. Then, since there are 55.5 mols of water in 1000 grams, the following simple proportion can be set up,

$$\frac{Ma_2}{55.5 - (X.Ms_2)} = \frac{Ma_1}{55.5 - (X.Ms_1)},$$

which gives, on solving for X,

$$X = \frac{55.5(Ma_2 - Ma_1)}{Ma_2Ms_1 - Ma_1Ms_2}.$$

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[1] Hostetter and Roberts: J. Am. Chem. Soc., 41, 1337 (1919).

Results and Discussions

The first four determinations were done with sugar solutions ranging from 0.9 to 1.9 molal, which were 1.58 molal in methyl alcohol. The degrees of hydration calculated varied between 0.6 and 11 molecules of water per molecule of sugar. The analyses were done by specific gravity methods, however, so that the probable error is very large.

The following table summarizes the results that we obtained with six different solutions, using alcohol concentrations of approximately 0.5, 1.5 and 3.5 molalities and sugar concentrations ranging from about 0.6 to 2.6 molality. In each case the alcohol was determined by oxidation.

Solution	Molalities		Hydration
	Sugar	Alcohol	
No. 1			
Original	1.66	1.53	
Filtrate (F)	0.95	1.58	2.4
Residue (R)	1.77	1.51	2.9
No. 2			
Original	1.201	1.518	
F_1	0.571	1.176	negative
R_1	1.352	1.483	"
F_2 (lost)	——	——	
R_2	1.412	1.462	
F_3	0.424	1.594	4.5
R_3	1.705	1.429	4.3
F_4	0.610	1.532	3.1
R_4 (thrown out)	(1.182)	(0.842)	
F_5	1.000	1.529	3.9
R_5	2.546	1.348	
No. 3			
Original	0.627	0.496	
F_1	0.329	0.489	negative
R_1	0.768	0.495	"
F_2	0.414	0.478	"
R_2	0.870	0.491	
F_3	0.477	0.488	"
R_3	1.041	0.496	
F_4	0.630	0.502	"
R_4	2.310	0.610	
No. 4			
Original	0.565	0.513	
F_1	0.180	0.475	"
R_1	0.634	0.511	
F_2	0.231	0.496	

Solution	Molalities		Hydration
	Sugar	Alcohol	
R_2	0.716	0.517	"
F_3	0.255	0.490	
R_3	0.838	0.518	"
F_4	0.336	0.508	
R_4	1.148	0.522	"
No. 5			
Original	0.796	3.40	
F_1	0.138	3.43	2.6
R_1	0.925	3.30	
F_2	0.170	3.46	3.1
R_2	(not sampled)		
F_3	0.100	3.46	
R_3	1.233	3.20	3.7
F_4	0.100	3.44	3.4
R_4	1.667	3.03	4.2
F_5	0.187	3.43	4.3
R_5	2.413	2.81	4.4
No. 6			
Original	1.199	0.502	
F_1	0.147	0.521**	
R_1	1.588	0.493	2.1**
F_2	0.851	0.498	0.7
R_2	2.058	0.496	0.2

* Same membrane as used in No. 5.

** This high value is attributed to insufficient washing of the membrane before adding the sugar solution.

In considering the data presented, one must bear in mind that all of the odds are against an increase in concentration of the reference substance in the filtrate with a corresponding decrease in the residue. Blank tests with methyl alcohol alone in water showed that there is almost always an increase in concentration above the membrane. This tendency to filter the alcohol out would be aggravated by the presence of the sugar molecules since the latter would tend to block the passages through the membrane as they are not able to get through freely themselves. The positive results, obtained in a direction to indicate hydration, occur in spite of other tendencies to the contrary, so that the figures obtained must be interpreted as minimum values. Almost certainly the actual hydrations are larger than our values.

With the dilute alcohol solutions, other influences are stronger than the tendency of the alcohol to concentrate in the filtrate, and no evidence of the hydration of the sugar is found. Just what the factor is that interferes more in the dilute solutions than in the more concentrated is as yet unknown to us. We feel certain, however, that the negative results obtained have in no wise vitiated the conclusion, drawn from the results as a whole, that in not excessively concentrated solutions of sucrose in water each molecule of sucrose on the average holds in some way not less than four molecules of water.

Since most of our filtrations were performed with thin membranes of nitrocotton superimposed on cellophane, it seemed plausible to us that the disturbance producing the negative results was closely connected with the character of nitrocotton. One of us, therefore, performed a filtration using a membrane made by filtering out viscose upon cellophane and converting the viscose to cellulose with acid. The sugar solution was made 0.5 molal with methyl alcohol. In spite of the different membrane, the analyses indicated zero hydration.

Summary

1. A method of measuring directly the degree of hydration of sucrose is described.

2. Data are given which indicate that sucrose in dilute solution is hydrated with not less than four molecules of water per molecule of sugar.

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THE EXISTENCE OF POTASSIUM ALUM IN THE SURFACE LAYER OF AQUEOUS SOLUTIONS*

BY E. ROGER WASHBURN

In a former article[1] attention was called to the crystalline deposit which often forms on the sides of a vessel above an evaporating, saturated, solution. An explanation was offered for this phenomenon. If the solution wets the walls with which it is in contact it will climb on them a little above the flat surface of the liquid. On evaporation, a crust is formed, separated from the material of the walls by a capillary space through which more liquid will rise, wetting the walls a little further. This process will continue until a height is reached, the same for all clean, wetted, surfaces; determined only by the surface tension of the solution and the diameter of the space through which it climbs, providing that the capillary layers do not become blocked by crystals growing together and in actual contact with the glass.

R. O. F. Oakley[2] calls attention to the fact that the phenomenon is discussed in a similar manner in Watts' Dictionary of Chemistry under the heading, efflorescence. The use of this term to cover phenomena of this kind is new to the author. Sulfur is not, I believe, usually thought of as being efflorescent, yet a deposit of sulfur will often form and creep above a solution of sulfur in carbon disulfide.

Hans Erlenmeyer[3] gives a detailed explanation of the phenomenon based primarily upon the failure of solutions of alums which he investigated to form a surface deposit and to spread upon the walls above the solution. The alums, he supposes, decompose when placed in water, potassium alum, for example, forming potassium sulfate and aluminum sulfate. These component salts in turn partially dissociate into their respective ions. The ions, tending to increase the surface tension of the solution, will according to the Gibbs' adsorption rule be negatively adsorbed at the surface; while the undissociated molecules lower the surface tension unequally and thus are concentrated at the surface in unequal amounts. If this be true, the composition of the dissolved material in the surface layer will not correspond to the composition of the double salt and no climbing of alum would be expected. Just why the simple salt which does predominate in the surface layer does not climb on the walls is not clear.

J. G. F. Druce[4] studied the amount of creeping shown by solutions of different salts and attempted to formulate a table showing their relative tendency to creep. His table is of interest because, of the eleven common

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* Contribution from the Chemistry Laboratory of the University of Nebraska.

[1] E. R. Washburn: J. Phys. Chem., 31, 1246 (1927).

[2] Private communication to the author.

[3] Helv. Chim. Acta, 10, 896 (1927).

[4] Pharm. J., 119, 333 (1927).

salts which he studied, he places alum fifth in the ability to creep, whereas Erlenmeyer claims that the alums do not form a crust at the surface at all. Druce does not state which alum he used, nor does he indicate whether or not he took pains to prove that the crust which he observed was alum.

It had been the experience of the author that alums did not differ essentially from other salts in ability to climb on the walls of the vessels although no attempt had been made to prove that the crust which formed was the double salt and not one of the component salts or a mixture of the components. The experiments have been repeated with this idea in mind with the following results.

Potassium alum, Mallinckrodt's C.P. quality, was purified by two recrystallizations from aqueous solution, was dissolved in water and the clear solution poured into crystallizing dishes which were then placed in desiccators above sulfuric acid. The crystallizing dishes had been carefully cleaned by successive treatments with hot alkaline permanganate, hydrochloric acid and hot water. They were then steamed thoroughly and dried in an electric oven. As expected from previous work a crust did form and spread on the glass walls above the solution. In some instances this crust was first noticeable after a day or two but in the majority of instances several days or a week elapsed before the deposit started to form. Crystallization often started at the bottom of the solution before the crust was seen on the walls. A study of some of the physical properties of the deposit from the walls was made in order to identify it as one or more of the following salts, alum, aluminum sulfate or potassium sulfate.

E. M. Chamot[1] gives the melting point of potassium alum as 92°C, and of potassium sulfate as 1070°C. The purified alum which we prepared melted at 91.7°C.; potassium sulfate was observed to melt in the neighborhood of 1000°C; while samples of hydrated aluminum sulfate were observed to lose the water of crystallization at 110°C. Samples of the deposit taken from above the evaporating solution of alum were observed to melt sharply at 91.7°C., not in the least distinguishable from the melting point of the purified salt used in the preparation of the solution.

Potassium alum crystallizes in the isometric or regular system, potassium sulfate in the orthorhombic system, while aluminum sulfate is monoclinic. Owing to the fact that the crust is composed of irregular, tree-like, crystal aggregates it is not easy to separate and identify the crystalline form of any single crystal. Also, the identification of the crystalline form of a few of the crystals would still leave open the question as to whether all the crystals in the crust were of the same crystalline form, and thus presumably of the same material. Observation of the dendritic mass between crossed nicol prisms should, however, readily enable one to distinguish between the optically isotropic crystals of alum and the anistropic crystals of either of its component salts. Investigation showed the crust to be made up entirely of iso-

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[1] "Elementary Chemical Microscopy," (1921).

tropic crystals, there being no change in luminosity when samples were rotated between crossed nicols. Samples of each of the simple sulfates when similarly investigated appear alternately light and dark as is characteristic of anistropic crystals.

The index of refraction of potassium alum as given by E. M. Chamot (loc. cit.) is 1.450. Observation through a microscope of samples of the crust immersed in turn in a series of organic liquids showed that the refractive index of the crystals was between that of chloroform (1.44) and that of carbon tetrachloride (1.46).

It is evident from the above investigation that potassium alum will form a crust at the surface of an evaporating solution and spread out on the walls above the solution. This does not necessarily mean that the decomposition of alum and the dissociation and preferential adsorption of the component salts as mentioned by Erlenmeyer does not take place. The decomposition of the double salt into its component salts undoubtedly takes place to a large extent in dilute solutions, probably to a much less extent in the saturated solutions used in these studies. The effect of inorganic solutes on the surface tension of water is usually very small, often they increase it slightly, but in no case would we expect very much adsorption, either positive or negative, of the salts at the surface. The effect of adsorption may easily be overbalanced by the effect of the evaporation of the more volatile component of the solution. For example, ethyl acetate in small amounts greatly lowers the surface tension of water, as is shown in the following table of surface tensions for different concentrations of ethyl acetate in water. In each of these cases the value given is the surface tension of the solution when it is in equilibrium with the vapor phase above the solution.[1]

Concentration	Surface Tension at 20.0 C ±.1	Lowering from water value
Molar /2	42.2 dynes/cm.	30.5 dynes/cm.
" /6	55.6 "	17.1 "
" /9	59.3 "	13.4 "
" /16	64.0 "	8.7 "
" /24	65.9 "	6.8 "
" /40	67.5 "	5.2 "

From the usual interpretation of Gibbs' adsorption rule ethyl acetate should concentrate in the surface layer and the surface tension of a freshly formed surface should decrease with time if this adsorption is the more important factor. The following table, typical of many studies made, shows the change of surface tension with time as observed with a half molar solution of ethyl acetate. The measurements were carried out in an open U tube type of capillarimeter at 20.0° ± .1°. The first reading was taken immediately after the solution was placed in the instrument and agitated. The solution was not agitated again until at the close of the run.

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[1] S. L. Bigelow and E. R. Washburn: J. Phys. Chem., 32, 321-353 (1928).

Time elapsed	Surface tension	Time elapsed	Surface tension
0 minutes	42.8 dynes/cm.	60 minutes	49.7 dynes/cm.
10 "	44.4 "	125 "	53.5 "
20 "	45.7 "	175 "	55.2 "
30 "	46.9 "	200 "	55.8 "
50 "	48.9 "	972 "	62.6 "

When the capillarimeter was closed so as to saturate the vapor phase the surface tension fell slowly to its equilibrium value of about 42.2 dynes/cm. The increase in surface tension has been interpreted by Bigelow and Washburn (loc. cit.) as due to the fact that ethyl acetate evaporates from the surface faster than it diffuses to or is adsorbed by the surface; thus the surface layer at each succeeding moment is more nearly pure water which shows its correspondingly higher surface tension. That the change in concentration thus brought about is confined to a very thin surface layer is indicated by the fact that after a maximum value of surface tension is reached in an open capillarimeter a violent agitation causes the surface tension to fall at once to very nearly its original low value, from which point a second rise will take place. This rise followed by a fall resulting from agitation has been repeated many times with the same solution with only a slight increase in the minimum value showing that the total loss of ethyl acetate by evaporation has been very slight.

H. M. Trimble[1] working with organic solvents as well as organic solutes observed the same phenomenon as described above and uses the same hypothesis to explain it. In addition, he observed with the system carbon-disulfide in toluene a fall in surface tension with time. This was to be expected for two reasons. The carbon-disulfide has a greater vapor pressure and a greater surface tension than toluene, thus a preferential loss of carbon-disulfide leaves a surface layer richer in toluene with its correspondingly lower surface tension. Also the toluene would be expected to concentrate by adsorption in the surface layer because it lowers the surface tension of the system.

Conclusions

1. It has been shown that a crust will form and spread on the walls above an evaporating solution of potassium alum. Evidence indicates that this crust is potassium alum.
2. Attention is called to other instances in which the effect of evaporation may overbalance the effect of preferential adsorption of surface active solutes at the surface of solutions.

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[1] J. Phys. Chem., 32, 1211 (1928).

THE SORPTION OF WATER VAPOR BY CELLULOSE AND ITS DERIVATIVES*

S. E. SHEPPARD AND P. T. NEWSOME

Introduction

The "regain" of moisture by different forms of cellulose has long been a matter of great practical as well as theoretical interest. With the extended development of cellulosic products in both textile and other industries this property assumes a wider interest, in regard to the numerous cellulose derivatives. Its theoretical importance for constitutional cellulose chemistry has been repeatedly emphasized by those great pioneers of cellulose investigation, Cross and Bevan.[1]

The present work is a contribution to the following problems:

a. Sorption and fine structure (micelle and crystal element).
b. Sorption and mechanical structure (porosity).
c. Sorption and chemical constitution (solvatation).

Experimental

The principal experimental results detailed are the adsorption and desorption isotherms, *i.e.*, the "moisture contents" in equilibrium with different vapor pressures at constant temperature. The apparatus used for measuring these has already been described by one of us,[2] but is illustrated here for the sake of completeness.

As shown in Fig. 1, it consists of a McBain-Bakr quartz fiber spring balance suspended in the adsorption vessel. The apparatus shown in the figure is placed inside a carefully controlled air thermostat.

Samples of the material are suspended from the calibrated spring and evacuated through *D* by means of an oil pump to constant weight at a pressure of 0.01 mm. of mercury. When *E* is opened, a small amount of the water contained in the capillary tube between *C* and *E* is admitted to the apparatus, thereby producing a definite pressure of water vapor. The weight of absorbed water is determined by the elongation of the spring as measured with a cathetometer. The pressure is measured directly with a cathetometer. When equilibrium is reached more water is admitted and a complete absorption isotherm thus obtained. Desorption curves are obtained by observing the equilibrium weights at different pressures as water vapor is removed through *D* by means of the vacuum pump.

It may be said at once that this apparatus transfers the chief difficulties in this work from the measurements of the sorption values to the preparation and definition of the materials. Cellulosic materials are by no means the

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*Communication No. 392 from the Kodak Research Laboratories.

most reproducible and readily characterizable known, to say the least. In consequence, one important result, perhaps the most important, of the present work consists in the conclusions arrived at in regard to defining the material more closely.

In general, the material was used in three main forms:

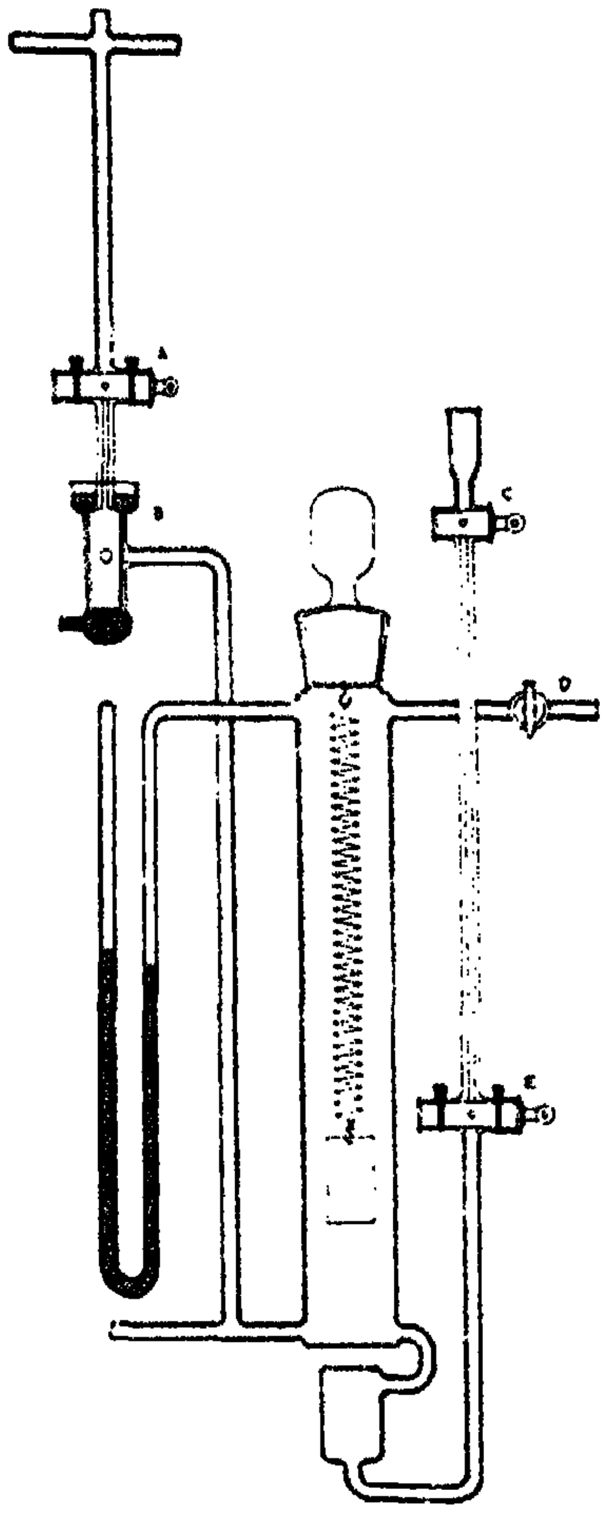


FIG. 1

a. as native fibrous material;
b. as dried precipitates or powders;
c. as thin sheets or films from solutions.

Not all the materials of interest can be prepared in all three forms. Native cellulose cannot be prepared in either the precipitated form, or as films, since, as will be noted later, it is questionable whether any process of solution can be effected on cellulose without denaturing it, that is, changing its internal structure.

The Adsorption Isotherm, and the Expression of Moisture Regain

Cellulose, and the cellulose derivatives considered in this paper, are not soluble in water, and therefore are substances with *limited swelling* in water. The amount of water adsorbed per gram increases, at a given temperature, with the vapor pressure present, to a maximum value for saturation. The most suitable or representative value for the "moisture absorption," on comparing different materials of this kind, would seem to be the maximum or limit value. While there is much to be said for this, and we shall so use it on occasion, it must be pointed out that considerable caution is necessary in regard to this value. That is because while the determination is most easily made in a *saturated* atmosphere, above liquid water, yet the value so determined is likely to be somewhat lower than the true value. The absorption increases very rapidly in the neighborhood of saturation, but an atmosphere above a liquid surface is usually completely saturated for only a very short distance above this,[3] or in small enclosures of metal.[4] Adjustment to the maximum may be effected by soaking in the liquid, but this is attended with the chance of error due to retention of mechanically retained liquid, an error which is least for smooth surfaces, as in gelatin plates or the like. However, the vapor pressures read on the manometer in our apparatus were equal to the saturation pressures of water at that temperature to within the error of reading. Since the manometer lay beyond the adsorption space, and the system was thermostatically enclosed, we consider that the values for the maximal adsorptions were very near the true values.

In comparing the "water adsorptions" of the different substances, we shall give the adsorption isotherms, and from these:

Adsorption at saturation	Adsorption at 50% R.H.	Integral adsorption

The integral adsorption is obtained by graphic integration of the adsorption isotherm over the whole range of vapor pressure.

The Moisture Regain of Cotton Cellulose

The raw fiber, or cotton sliver, contains waxy and other bodies which affect the water adsorption. Measurements were made on *Standard cellulose*[5] prepared by the Organic Research Department of this Laboratory, as well as on good grades of *cotton linters*, which were used to prepare the cellulose derivatives. These had been given an alkaline kier treatment, and had been slightly bleached with chlorine. The α-cellulose content of these linters was above 90 per cent; fat and wax, 0.5 per cent. The somewhat lower values might be due partly to residual waxy material, but it was also found that an *oxy-cellulose* and a *hydrocellulose* had lower adsorption values than either standard cellulose or cotton linters.

The sample of oxy-cellulose was prepared by Mr. Murray, of the Organic Research Department of this Laboratory, by treatment of the cotton linters cellulose with potassium dichromate in normal phosphoric acid for six hours at 52°C., followed by thorough washing. The sample of "hydrocellulose" should perhaps be more properly termed a degraded cellulose, since it was not prepared by treatment with aqueous acid, but by digestion of the cotton linters cellulose with nearly glacial acetic acid containing 2.5 per cent by weight of strong sulfuric acid (100.4% H_2SO_4) at 30°C. for three hours with powerful agitation. It was then thoroughly washed to remove all traces of acid, dried and pretreated twenty-four hours at 105° C. Although in the form of a fine soft powder, and containing a little fixed sulfuric acid (0.80 per cent) it will be seen that its adsorption is much less than that of the original fibrous material.

There is some evidence, which will not be stressed at this time, that the moisture regain, or water adsorption, of cellulose is progressively lowered by treatments which degrade the cellulose. In Table I are given the viscosities in cuprammonium solution 2.0 per cent cellulose, in 3 per cent copper in 16.5 per cent NH_3, and the maximum moisture regain of these cotton celluloses. Since the "hydrocellulose" was reduced to a powder, its external dispersity was considerably greater than that of the fibrous materials, and the change of moisture regain must be referred to some reduction of inner dispersity. The following table and curves give the data on the water adsorptions found for these materials.

TABLE I

	Viscosity	Moisture Regain
Standard cellulose	40,000	17.5
Cotton linters	4,800	15.0
Hydrocellulose	10	10.37

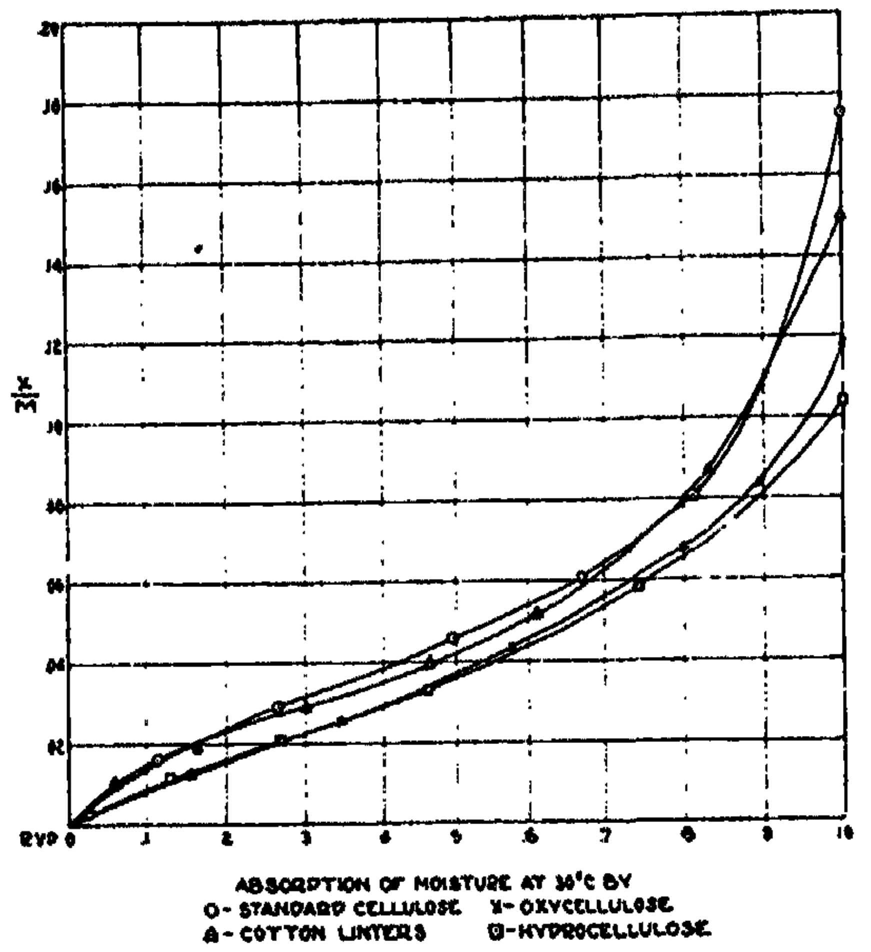


FIG. 2

TABLE II

Standard Cellulose		Cotton Linters		Oxy-cellulose		Hydrocellulose	
p/P	x/m	p/P	x/m	p/P	x/m	p/P	x/m
0	0	0	0	0	0	0	0
0.027	0.0029	0.059	0.0107	0.153	0.0124	0.131	0.0113
.116	.0162	.162	.0191	.344	.0253	.269	.0204
.266	.0290	.300	.0290	.575	.0433	.459	.0331
.497	.0458	.463	.0401	.800	.0676	.747	.0583
.669	.0603	.609	.0519	.894	.0836	.900	.0810
.809	.0806	.828	.0870	1.000	.1187	1.000	.1039
1.000	.1751	1.000	.1497				

Mercerization and Hydrate Cellulose

Cellulose, such as cotton fibers, mercerized by soaking in strong solutions of caustic alkalies,—15 per cent and upward—and then washed to complete removal of the alkali, is known to have changed properties. The underlying cause for these changes will be noted shortly. In particular, the water adsorption or moisture regain is considerably increased.[6] This was confirmed by our measurements (see Table III and Fig. 3). We have also determined the absorption of water vapor by *cellulose regenerated* from cuprammonium by precipitation respectively with sulfuric acid and by alkali, followed by thorough washing, and by *cellulose regenerated* from cellulose acetate by careful de-esterification with 1/2 N – NaOH solution. (See Table III and Fig. 3.)

TABLE III

Standard Cellulose		Cotton Linters		Hydrate Cellulose A		Hydrate Cellulose B		Hydrate Cellulose C	
p/P	x/m	p/P	x/m	p/P	x/m	p/P	x/m	p/P	x/m
0	0	0	0	0	0	0	0	0	0
0.027	0.0029	0.059	0.0107	0.030	0.0056	0.062	0.0057	0.062	0.0163
.116	.0162	.162	.0191	.091	.0156	.150	.0137	.169	.0370
.266	.0290	.300	.0290	.175	.0296	.378	.0621	.325	.0636
.497	.0458	.463	.0401	.378	.0552	.591	.0998	.509	.0894
.669	.0603	.609	.0519	.584	.0808	.875	.1635	.681	.1187
.809	.0806	.828	.0870	.678	.0964	1.000	.2347	.864	.1702
1.000	.1751	1.000	.1497	.816	.1245			1.000	.2657
				1.000	.2269				

In this table, hydrate cellulose A was material prepared from cotton linters by twenty-four hours' soaking in 20 per cent NaOH solution at room temperature, followed by thorough washing. Hydrate cellulose B was cellulose regenerated from cuprammonium solution, while hydrate cellulose C was cellulose from de-esterified cellulose acetate. It will be seen that the moisture absorptions of these materials are nearly alike, and much higher than that of normal cellulose. This difference is not due to any factor for molecular aggregation (polymerization), as can be seen on comparing the cuprammonium viscosities.

Material	Viscosity
Standard Cellulose	40,000
Cotton Linters	4,800
Hydrate Cellulose A	2,028
Hydrate Cellulose B	51
Hydrate Cellulose C	5.6

"Mercerized" standard cellulose has its viscosity somewhat lowered compared with untreated cellulose, but can have a much higher viscosity than a "normal" cellulose which has been degraded by acid treatment. Yet the latter has if anything a lower moisture absorption. The regenerated celluloses had extremely low viscosities, yet their moisture absorptions were equal to that of mercerized cellulose.

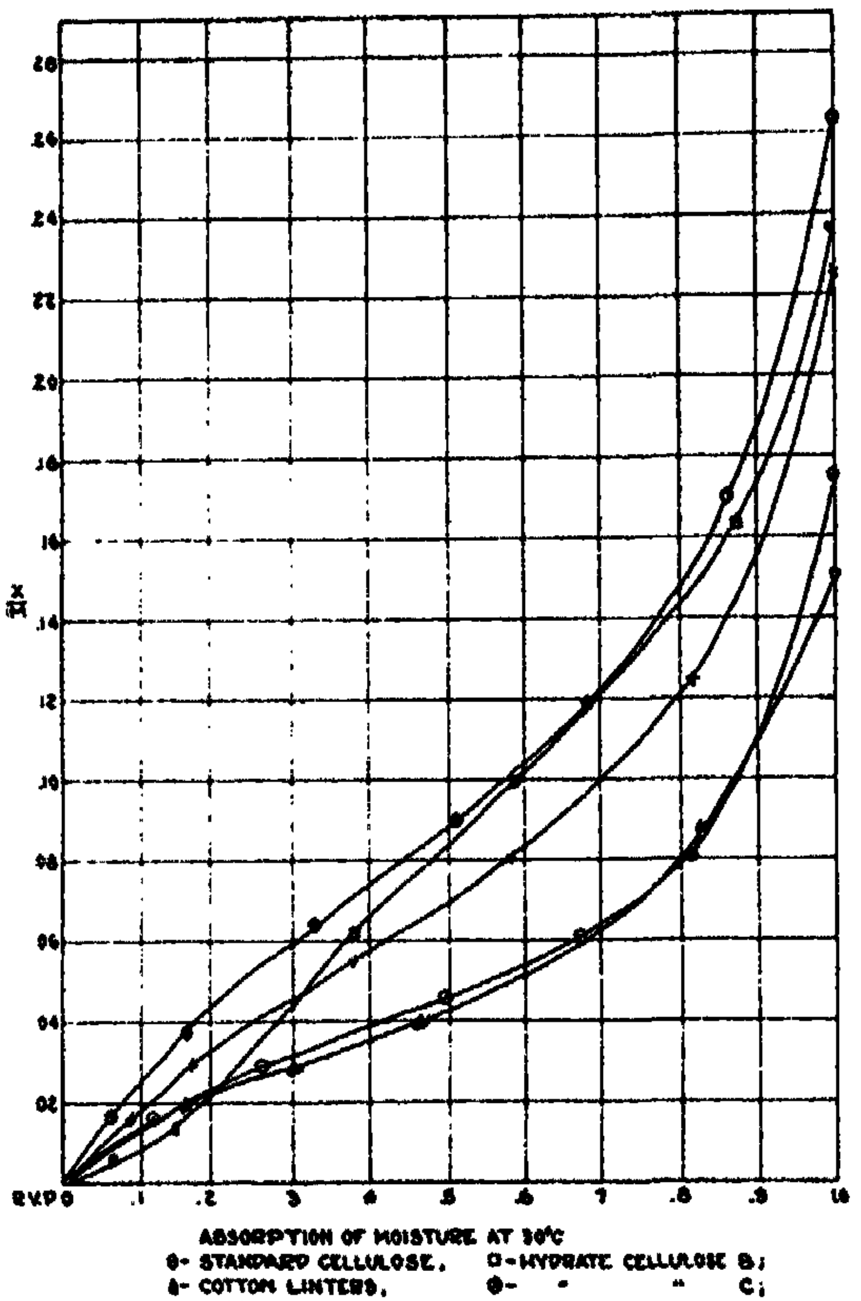


FIG. 3

Fine Structure of Cellulose

These results are in good agreement with what has been learned by X-ray spectroscopy of the fine structure of cellulose, *i.e.*, concerning the arrangement of its atoms and atomic groups in crystalline order. There appears no reason for regarding "mercerized" or "hydrate" cellulose as differing in chemical composition or constitution[7] from normal or "native" cellulose.[8] Again if we express the molecular aggregation, or degree of polymerization, by the expression $(C_6H_{10}O_5)_n$, there is no evidence that the moisture adsorption depends upon the degree of aggregation expressed by n, at least in so far as the cuprammonium viscosity is a measure of this value. On the other hand, X-ray spectroscopic examination has shown that there is a definite and characteristic difference between the fine structure of normal cellulose and that of hydrate cellulose.[9]

The investigations of R. O. Herzog, M. Polanyi, and collaborators, of O. L. Sponsler and W. H. Doré, and more recently of K. H. Meyer and H. Mark,[10] have led to a fairly definite conception of the fine structure of cellulose and its derivatives. While ramie fibers give a well marked fiber diagram, cotton cellulose fibers give only powder diagrams with singularities indicating some approach to a fiber diagram. The evidence is to the effect that in both these, and other varieties of native cellulose, the fundamental basis cell and the spatial arrangement of the atom groups in the crystallites are the same, but that whereas in ramie the crystallites are to a large extent similarly oriented in the direction of the fiber axis, in cotton cellulose the ordering of the crystallites is less symmetrical,[11] and regular.

The interpretation of X-ray data for cellulose which is most consistent with both the spectroscopic and the chemical data is that of Meyer and Mark.[12] This leads, for normal cellulose, to the conclusion that the crystallites are formed of long primary valence chains of glucose anhydride units glucosidically bound by 1:4 α-linkages, as in cellobiose. Haworth's constitution for cellobiose is accepted, and the glucose anhydride unit is given the pyrazone or hexagonal ring form proposed by Haworth. The pyrazone rings are ordered in the direction of the fiber in the form of a digonal screw axis. (*Cf.* Fig. 4.) This crystalline part of the cellulose gives a fiber diagram from which is derived a basis cell of the dimensions

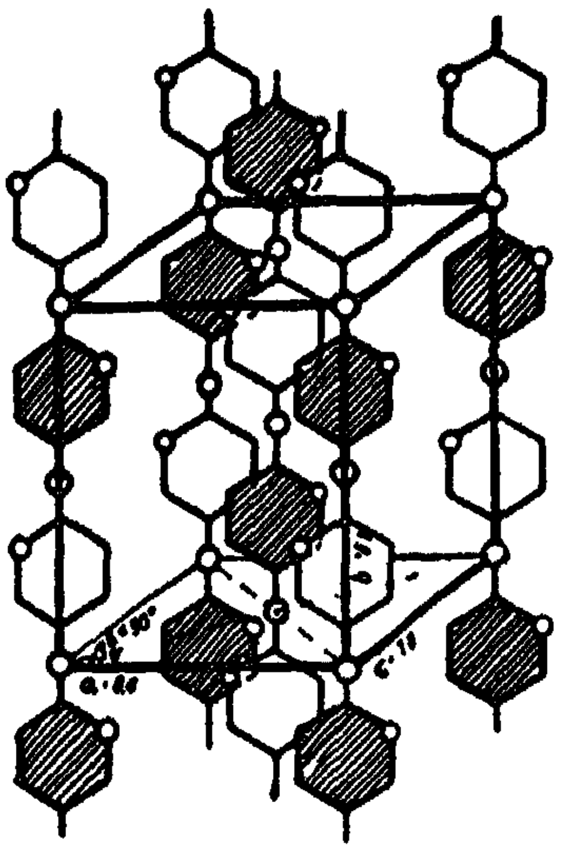


FIG. 4
Spatial arrangement of the cellobiose chains in the elementary cells. The shaded and unshaded hexagons (hexosan units) form digonal screws about the b-axis.
Meyer and Mark: Ber., 61, 593 (1928).

a. 8.7 Å.U.
b. 10.3 Å.U. (Fiber axis)
c. 7.9 Å.U.

The smallest possible cell has 4 ($C_6H_{10}O_5$) units. There is no necessary relation of the unit cell to the *molecular* weight or limit of these primary valence chain lattices. While the union along the fiber axis is by primary valence of the —O— bridge, the association of the chains is by secondary valences or van der Waals' forces. The basis cell corresponds to a rhombic crystal symmetry.[13]

Comparison of "native" and "mercerized" or hydrate cellulose shows that the latter gives small but definite displacements of the points of the fiber diagram.

TABLE III
Equatorial Points

Point		Method I		Method II		Index
Native	Hydrate	Native	Hydrate	Native	Hydrate	
A_4	B_4	0.195_0	0.192_8	0.194_7	0.192_1	002
A_3	B_3	$.176_0$	$.172_7$	$.176_4$	$.171_8$	200
A_2	—	$.142_3$	—	$.142_7$	—	$10\bar{1}$
A_1	B_1	$.133_4$	$.124_3$	$.133_2$	$.124_8$	$10\bar{1}$
	B_0	—	$.101_6$	—	$.100_9$	[1001 [100

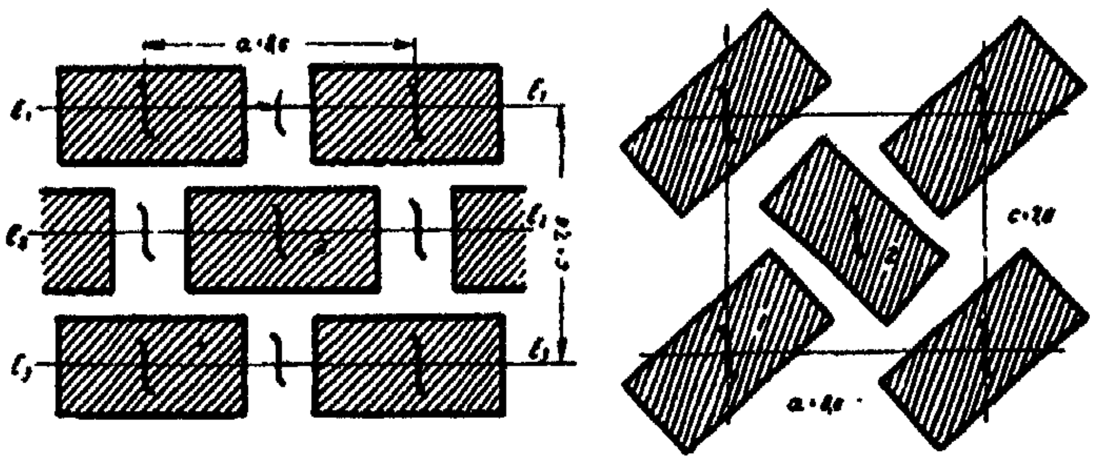


FIG. 5
Native Cellulose Lattice Hydrate Cellulose Lattice
Meyer and Mark: Ber., 61, 593 (1928).

The points of the "hydrate" diagram correspond to a basis cell of rhombic or slightly monoclinic symmetry of

a. = 8.90 – 8.95 Å.U.
b. = 9.95 – 10.05 Å.U. (fiber axis)
c. = 8.02 – 8.10 Å.U.

That is, they show a *contraction* in the fiber direction, and a dilation in the two other directions at right angles thereto.

The conclusion is reached that the most important characteristics of the hydrate cellulose are accounted for if the hexosan units are so rotated with respect to each other that their planes become approximately perpendicular to each other. "As the basis cells are at the same time somewhat separated in both directions, mercerization involves a slight pushing apart of the formerly co-chained cellobiose threads, accounting for the higher reactivity."

This conception is illustrated by the two diagrams in Fig. 5 reproduced from Meyer and Mark's paper.

The conclusion that mercerization involves only a rearrangement inside the basis cell is supported by R. O. Herzog.[14] It is agreed by both Meyer and Mark, and by Herzog, that the hydrate cellulose lattice represents more stable, less energy-rich arrangements; the native cellulose lattice a more deformed, less stable modification.

The hydrate cellulose lattice is formed by actual invasion of the basis cell by sodium hydrate molecules,[15] and after removal of the alkali, permits intra-crystallite, or intra-micellar absorption of, or swelling by, water and other polar molecules.[16]

Fine Structure and Sorption

The "fine structure" differences between native and mercerized cellulose therefore afford a reasonable basis for accounting for the increased sorption of water vapor by the hydrate cellulose. In part this might be accounted for by the increase of internal dimensions of the basis cell, but to consider the volume is only one way of envisaging the facts. It must also be considered that in the hydrate cellulose the hydroxyl groups of the cellulose are less mutually satisfied, so that their attraction for foreign polar molecules, capable of dipole orientation, is increased. We shall return to this point on considering more generally the factors determining the sorption.

"Hydrocellulose" and oxy-cellulose have no different X-ray spacings from those of native cellulose.[17] The only indications at present as to their "fine structure" is that the similar orientation of the crystallites is reduced, and the proportion of an amorphous phase[18] is increased. The lowered water absorption compared with native cellulose is accountable either on the view that disorientation has permitted still greater increase of the mutual attraction of the hydroxyls, or that the pore space has been diminished. On the other hand, the identity of the water adsorptions of regenerated celluloses with that of mercerized cellulose, which is in agreement with the X-ray investigation of these substances,[19] is of great importance.

Esterification and Sorption

The importance of the free hydroxyls of cellulose for the sorption of water is shown by the well known fact of the great diminution of water adsorption produced by nitration, esterification, or ether formation. Since these substances still have an appreciable water adsorption, it becomes of importance to consider this, as well as the relation of the sorption to the degree of esterification.

In studying the sorption by cellulose esters of organic acids, *e.g.*, of cellulose acetates, it must be noticed that *a priori* we have two series of these, according as they are prepared by fibrous esterification, *i.e.*, the cellulose is never dissolved in the esterification mixture, but maintains its fibrous form, and secondly those in which the cellulose (or rather the ester) is dissolved in the reaction mixture.[20] Cellulose nitrates are uniformly made by the first procedure, while cellulose acetates may be made by either, but practically for certain reasons are usually prepared according to the second. It must be noted, however, that there is little if any principal difference in the primary process of esterification between the two. In either case the esterification is a topochemical reaction accomplished by reaction in the solid phase, which is only "dispersed" or dissolved in the acetylating mixture (acetic acid plus acetic anhydride plus mineral acid) when some 40 per cent acetyl has been fixed.

The chief differences between the primary heterogeneous reactions in the two cases are in the uniformity of acetylation of the fibrous solid.[21] In the second case, where the acetylation product goes into solution, the unacetylated material is progressively exposed to further attack. In the former case, complete pseudomorphosis may be accomplished[22] giving a cellulose nitrate or acetate fiber which shows a "fine structure" of the same

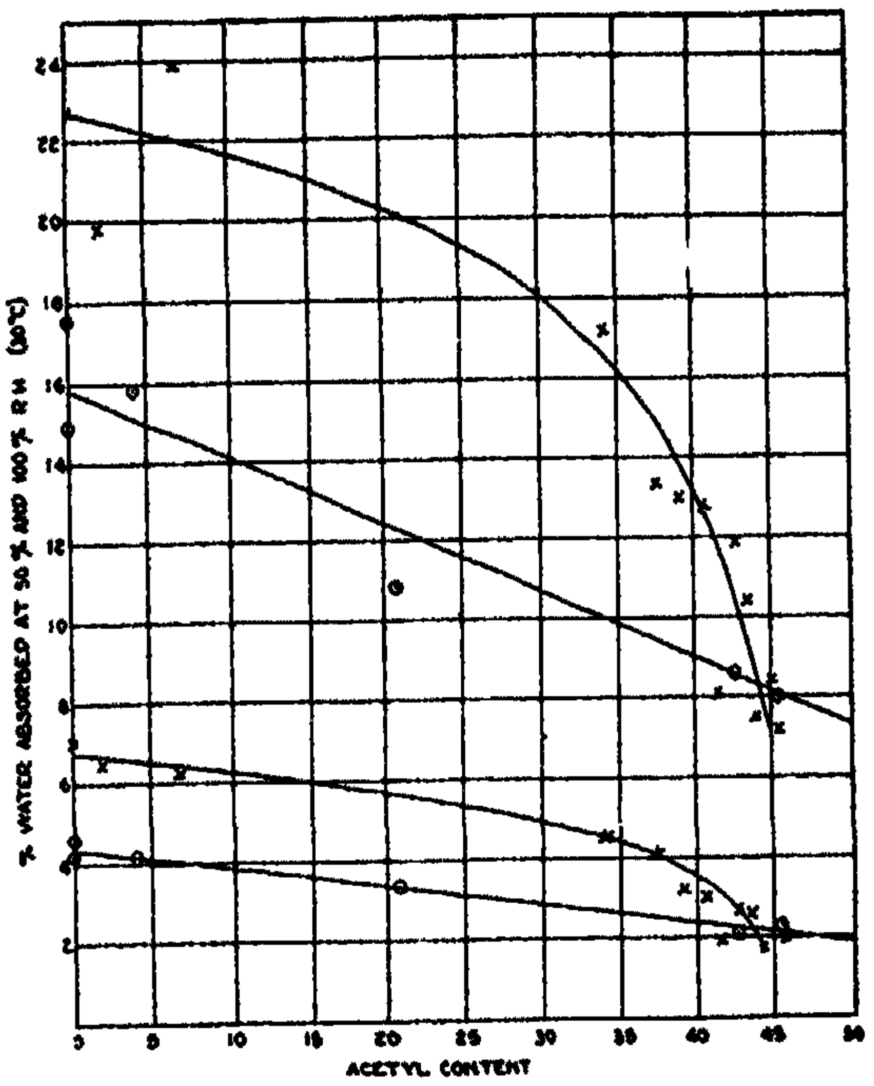
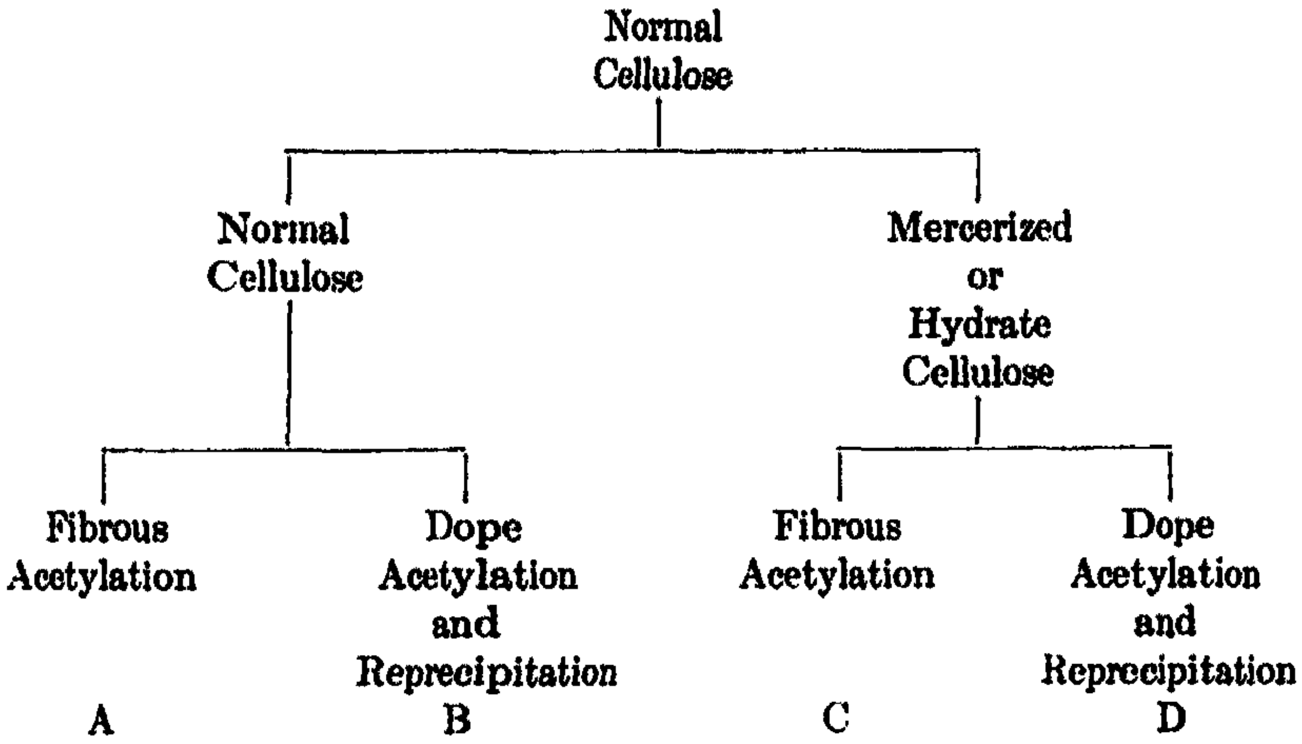


FIG. 6

lattice system as that of normal cellulose.[23] On the other hand, cellulose actates prepared by the second procedure, *i.e.*, having passed through solution, followed by precipitation in some form, show evidence of a different "fine structure," and when carefully de-esterified were found by R. O. Herzog and his collaborators[24] to give the diagram of "hydrate" cellulose.

It appears not only that in any solutions in organic solvents (acetic acid, acetone, etc.) the fibers are dispersed at least to the crystallite building blocks, but that the solvent penetrates the crystallites themselves, and enlarges the basis cell, in the same way that caustic alkalies penetrate in mercerization, and enlarge the basis cell of cellulose itself. In fact evidence has been given by Sheppard and collaborators[25] that in sufficiently dilute solutions this "solvating" effect extends to complete splitting up of the crystallite into molecular threads, so that recovery from these solutions of material giving the fine structure of mercerized or hydrate cellulose means that there is a real recrystallization.[26]

It will be seen that our results for the water adsorption of de-acetylated cellulose acetate are in good agreement with the deductions from X-ray data. We have been able, however, to push the correlation somewhat further than this. There can be prepared the following series of cellulose acetates, using series in the sense of progressive degrees of acetylation:



The "fine structure" and moisture adsorption of series B, C, and D should by and large agree with each other, and differ markedly from those of series A. It has not been possible yet to complete the data on these four series, but the data plotted in Fig. 6, and shown also in Fig. 7 indicate that:

a. Cellulose acetates made from normal (unmercerized) cellulose by fibrous acetylation and not put into solution form a series in which the moisture regain decreases as the acetyl increases. The relation appears to be linear. In the case of the nitrates examined by Will[27] he found the moisture absorption given by the equation

$$W = \frac{334.4 - 23.65\,N}{31.11 - N}$$

where N = per cent nitrogen, but our data for this series of acetates are insufficient to determine whether a simple linear form of the type $W = a - b\,A$ is sufficient.

b. Cellulose acetates made from mercerized (hydrate) cellulose, by fibrous acetylation, or from normal cellulose, but put into solution and reprecipitated, form another series of cellulose acetates of higher moisture regain. This series, however, rapidly converges to meet the lower series as the acetyl content approaches that for the triacetate (44.6% acetyl).

The difference in moisture regain between these two series we consider to be due to the intra-micellar or intra-crystalline absorption of water.

If we consider that the precipitated triacetate has also the modified "hydrate" cellulose lattice (Fig. 5) then the agreement of the moisture regain of this material with that of fibrous triacetate from normal cellulose, which must be assumed to have the normal lattice, indicates that the chief importance in the change of lattice structure consists in the relative freeing of *hydroxyl* groups, so that they can exercise their full attraction for water or polar solvents.

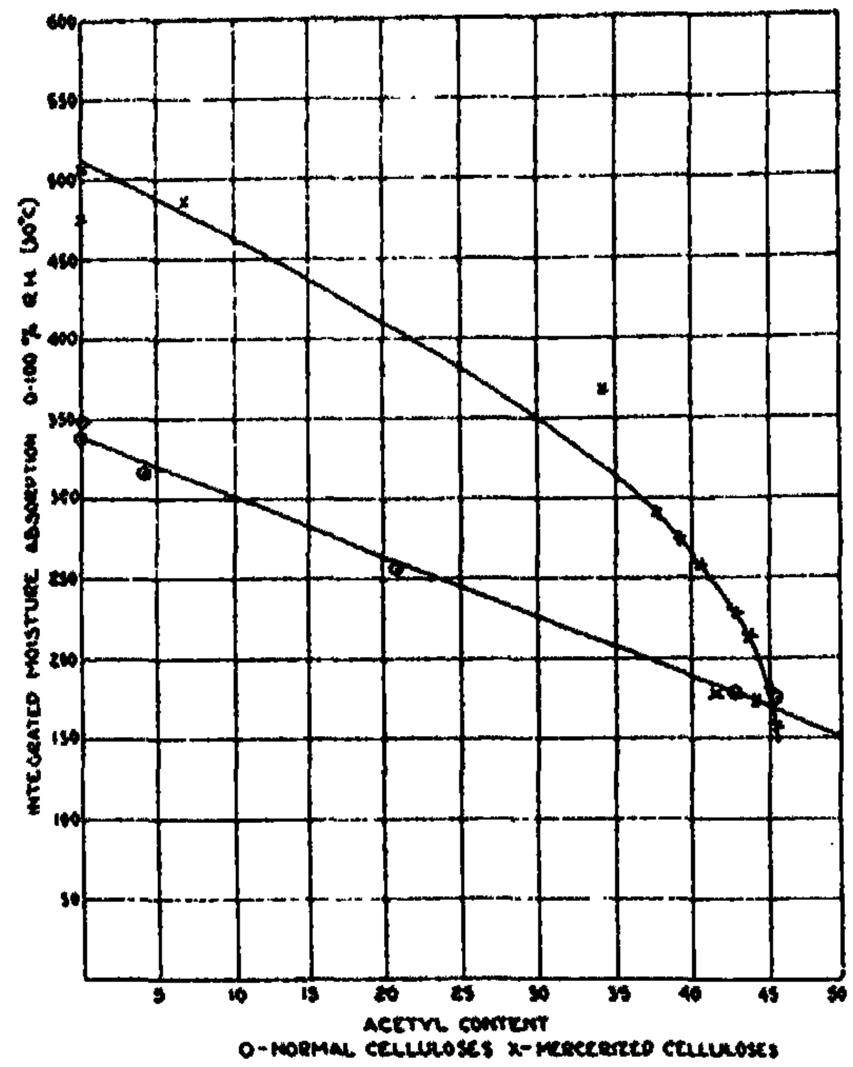


FIG. 7

Inter-micellar Adsorption

Although the complete acetylation of cellulose to triacetate greatly reduces the water adsorption, yet it leaves it considerably higher than might be expected after esterification of the hydroxyls. Thus the complete acetylation of glucose to glucose pentacetate, and of cellobiose to cellobiose octacetate reduces the moisture absorptions to the very small amounts of 1 to 2 per cent at 100% R.H. (see Fig. 8). [redacted]

It appears from this, as well as from other evidence, that a considerable part of the total moisture regain by cellulose and its esters must be due to the structure of the gel, *i.e.*, to inter-micellar adsorption by ultra-microscopic capillary spaces or micro-pores. In the case of cellulose nitrate sheets—so-called collodion membranes for dialysis and ultra-filtration—it has long been known[28] that the porosity of these could be controlled in large measure by incorporation of inert, *i.e.*, non-solvent substances in the solution, previous to coating and drying the membrane, these substances being usually leached out in the subsequent treatment. Membranes of "controlled" porosity—to a certain degree—were prepared in this way. We propose to deal with the behavior of these in a later communication, and will refer here to only one case of such modified porosity.

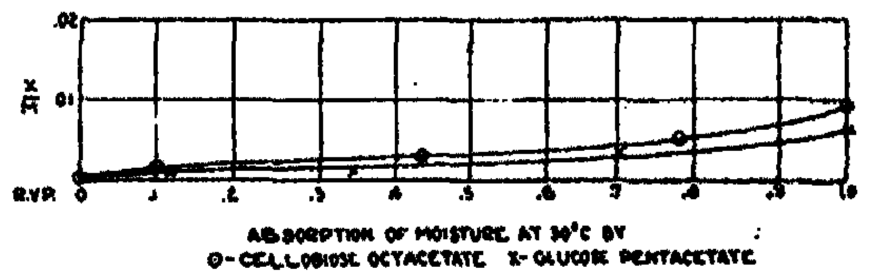


FIG. 8

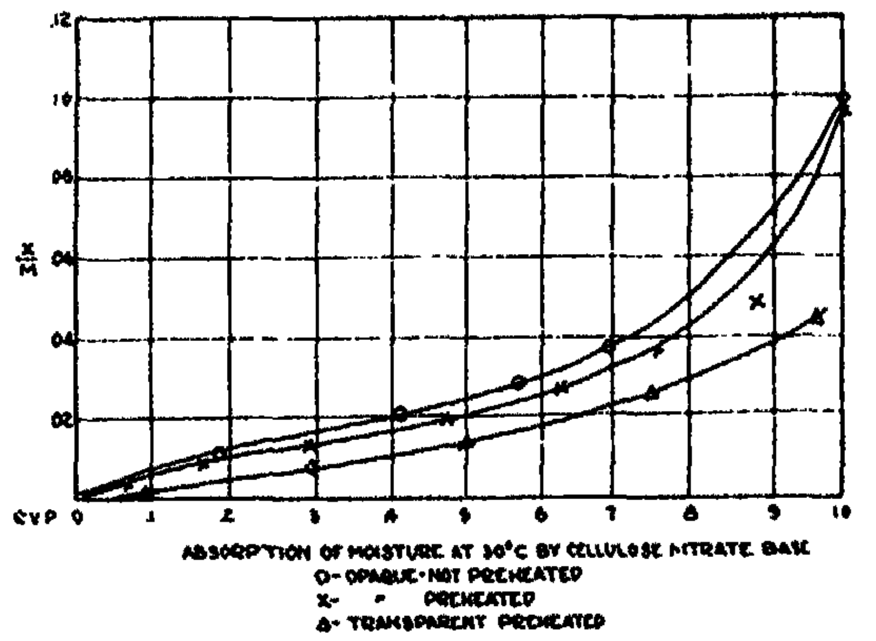


FIG. 9

If a cellulose nitrate dissolved in acetone is allowed to evaporate in an atmosphere containing considerable water vapor, or is set in water, it is well known that an opaque white film is produced. Such films have a microscopically porous structure similar to meerschaum. We have compared the moisture absorption of such a cellulose nitrate film with that of the same material dried out in transparent form. The data are shown in Fig. 9 and Table IV.

It will be seen that the opaque material showed much greater absorption than the transparent material. The lowering of the adsorption by pretreating at 105°C. is possibly due to the collapse and sealing up of certain pores. Since both the transparent and the opaque material were prepared from the same cellulose nitrate, of 10.8%N, it is evident that the difference in adsorptive power is due solely to the gel structure.

According to Lord Kelvin's equation[29] for the influence of curvature on the vapor pressure of liquid drops, the radius is proportional to the relative vapor pressure, and a high pore radius, and conversely. The pore radii were calculated according to this equation.

$$r = \frac{\sigma}{2\rho T \ln \frac{L}{p/P}}$$

where

r = pore radius

σ = surface tension of adsorbed water—assumed constant and equal to that of pure water 71.4 dynes/cm. at 30°C.

R = gas constant = 4.61×10^6 C. G. S.

ρ = density of adsorbed water—assumed constant and equal to that of pure water = 0.99567 at 30°C.

T = absolute temperature = 303°.

Hence, taking numerical values

$$r = \frac{0.4458 \times 10^{-7}\ \text{cm.}}{\log \frac{1}{p/P}}$$

Using this expression, we obtained the following table:

TABLE V
Relation of Moisture Adsorption to Pore Radius

		Opaque not Preheated		Opaque Preheated		Transparent Preheated	
p/P	r (in mμ)	x/m	Q	x/m	Q	x/m	Q·
0	0	0	0	0	0	0	0
0.001	0.1486						
.01	.2229						
.025	.2783						
.05	.3427						
.1	.4458	0.00675	6.88	0.00565	5.88	0.0027	5.71
.2	.6379	.0120	12.24	.01015	10.56	.0053	11.35
.3	.8527	.0163	16.62	.01355	14.10	.00815	17.45
.4	1.1204	.0205	20.91	.0170	17.69	.0110	23.55
.5	1.481	.0250	25.49	.0212	22.06	.0141	30.19
.6	2.010	.0304	31.00	.02625	27.32	.0178	38.11
.7	2.878	.0374	38.14	.0325	38.93	.0230	49.25
.8	4.601	.0485	49.46	.0402	41.84	.0296	63.38
.9	9.743	.0669	68.22	.0512	53.29	.0374	80.09
.95	20.01	.0807	82.29	.0634	65.99	.0419	89.72
.98	50.83	.0906	92.39	.0777	80.87	.0458	98.07
1.00	—	.09806	100.00	.09608	100.00	.04670	100.00

Column 1 of Table V shows selected values of the relative vapor pressure from 0 to 1 and column 2 the corresponding values of the pore radii calculated. Columns 3, 5, and 7 give the values of the adsorptions corresponding. In Fig. 10 is shown the variation of adsorption with "pore radius" using data from Table IV. The curves in this have the same general form as the theoretical curve of the function

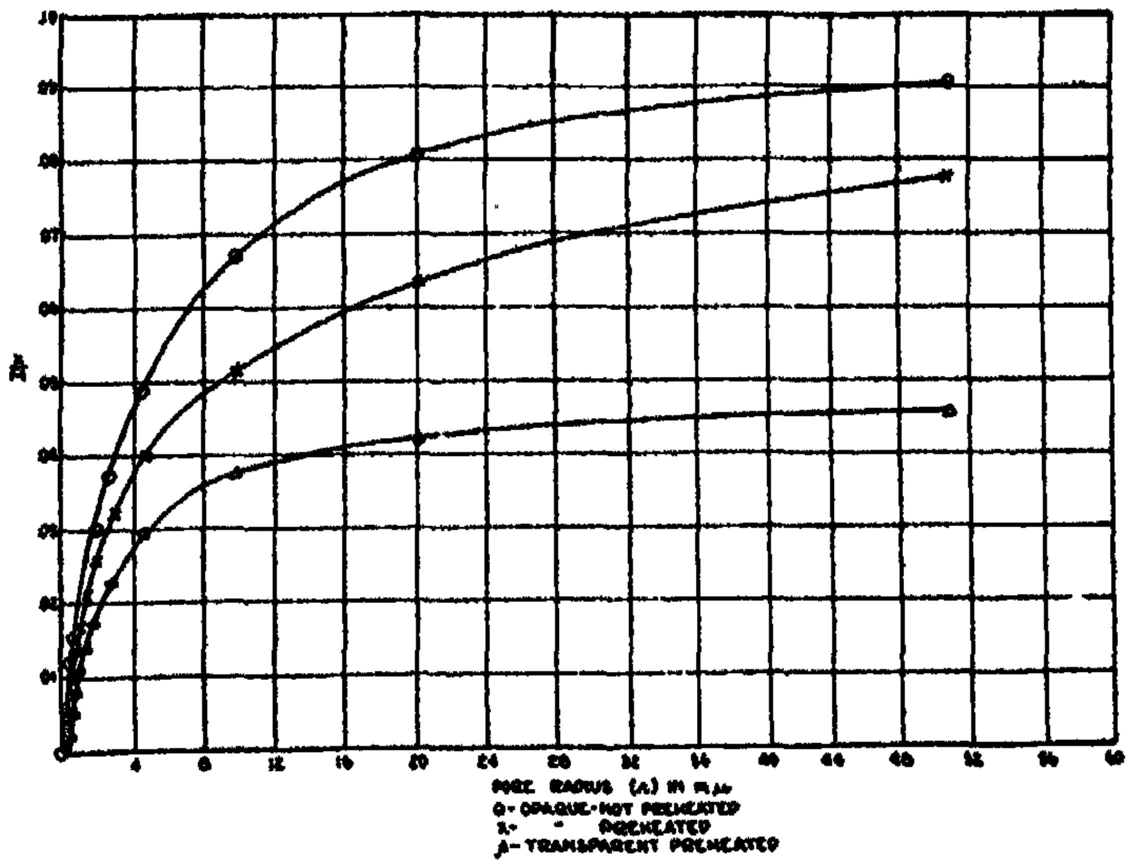


Fig. 10

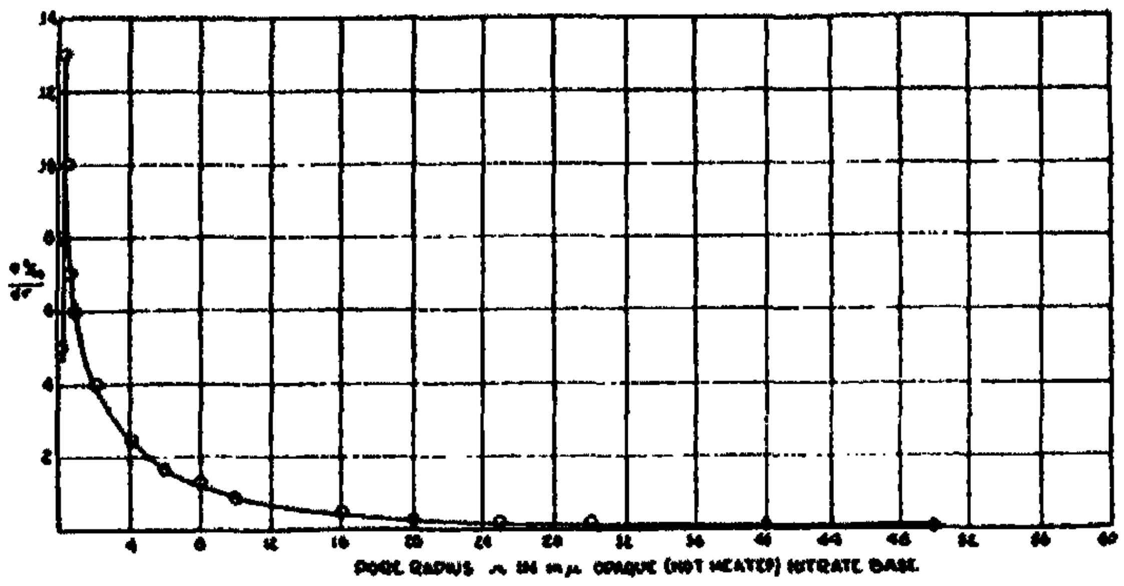


Fig. 11

$$\frac{2\,\sigma}{R\rho T \log \frac{1}{p/P}}.$$

In order to obtain the distribution of pore sizes, we may plot $\frac{d\,x/m}{dr}$ as a function of r, or of log r. Figs. 11 and 12 show distribution curves obtained in this manner. Plotting as *f* (log *r*) is more satisfactory when the most frequent pore is small.

J. S. Anderson[30] investigating the sorption of liquids by silica gel stated that only points on the desorption curve should be used to calculate the pore radii because of incomplete wetting of the walls in adsorption. This will be noted in dealing with hysteresis but it may be stated that a later calculation from desorption data with cellulose acetate showed that the general shape of the distribution curve, and the value of the most frequent pore size were not materially altered.

The most frequent pore size from the data is of radius 5 Å.U. or 10 Å.U. diameter. This value is not so very much larger than that of moderate sized molecules, and can hardly be significant in the case of small molecules such as water, alcohol, etc.

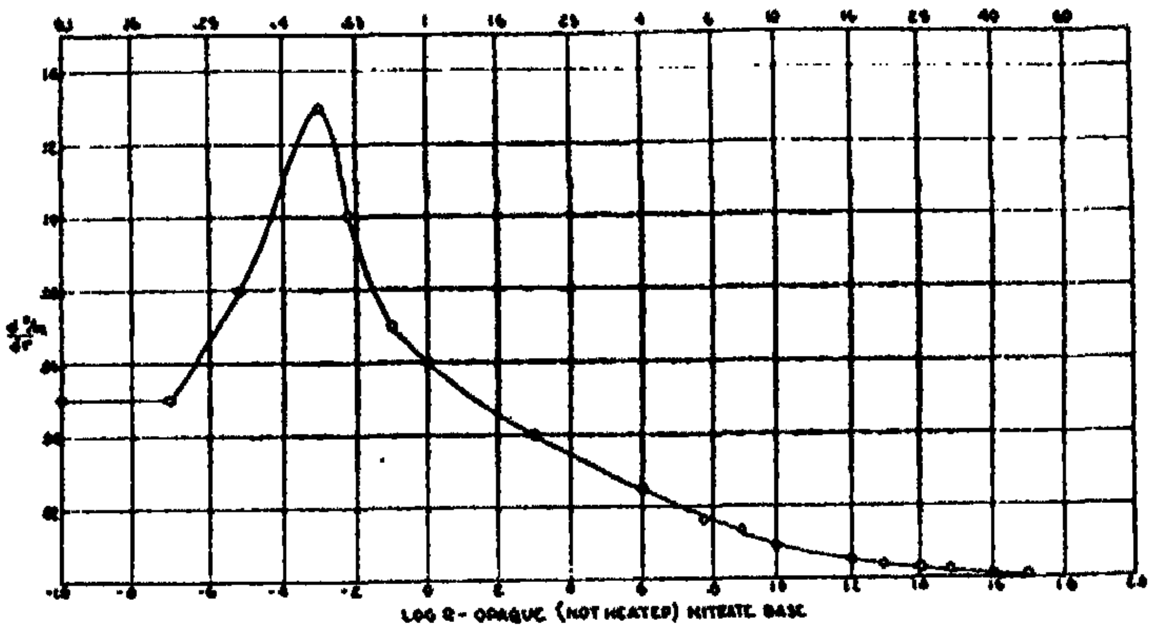


FIG. 12

Substance	Molecular diameter
H_2O	5.6 Å.U.
C_2H_5OH	6.0. Å.U.

Hence, there is a considerable possibility that the capillary adsorption ceases to be valid for small vapor pressures, corresponding to pore radii below a certain value.

Sorption Hysteresis

All of the cellulosic materials studied showed sorption hysteresis. That is, on desorption, the moisture contents at given vapor pressures intermediate between 1 and 0 are higher than on adsorption. On repeating the adsorption and desorption, a new cycle is established. (See Fig. 13.) Repetition of the sorption cycle (adsorption → desorption) led to a reduction of the hysteresis, or narrowing of the hysteresis cycle. This was less marked with the precipitated or powdered material than with the dried sheet or film.

Various explanations have been given of this phenomenon. In terms of the pore theory, on the first explanation, desorption is due to evaporation from the curved surfaces in the pores. On adsorption, or filling, the wetting is supposed less complete, the contact angle, if any, greater, and therefore, the vapor pressure for a given amount is higher; according to this hysteresis should be largely confined to the steepest part of the curve. This is not entirely true with our material, although the area of the hysteresis cycle is somewhat larger for the steeper part of the curve. According to the second explanation the hysteresis is ascribed to air in the pores interfering with their wetting and filling. Patrick[31] found with silica gel that thorough evacuation could largely eliminate such hysteresis. This does not seem adequate with our material, since the absorbent was repeatedly evacuated to a pressure of 0.005 mm., and yet hysteresis, though reduced, was still quite apparent.

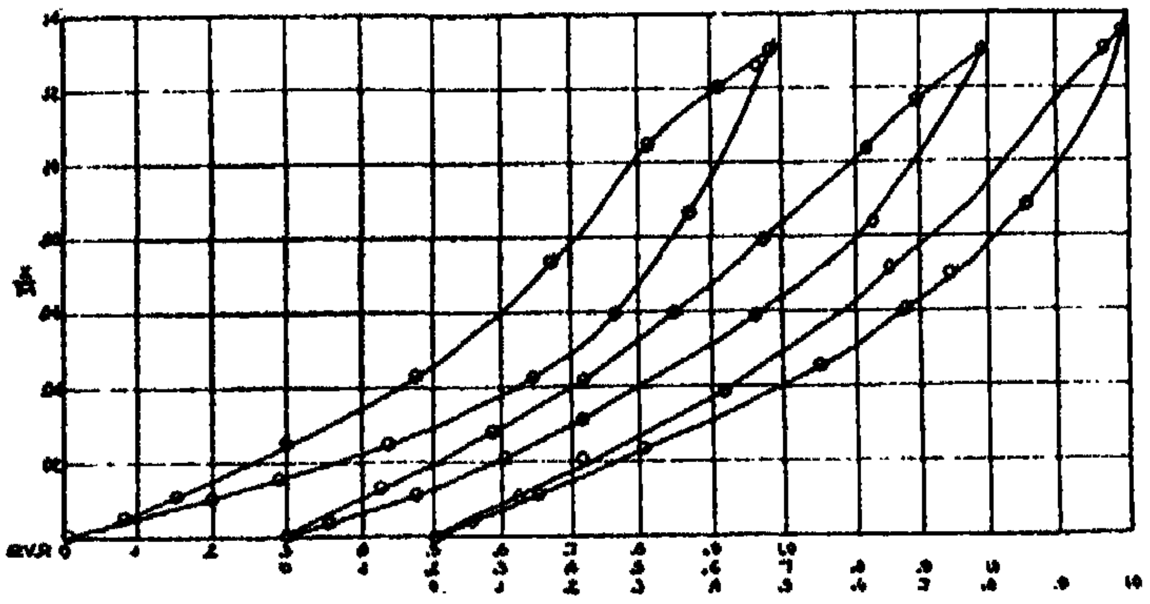


FIG. 13
Repetition of Hysteresis Cycles

J. McBain[32] and Ferguson have offered a third explanation, in the case of building materials (Gatton stone, etc.) which they have also applied to cellulose nitrate. They found that evacuating four times to 0.00001 mm. still gave hysteresis. They found that even these "rigid gels," as silica gel, show some "swelling" on adsorption. This they attributed to "uncoupling of certain linked particles—through addition of a molecule of water to each valency bond broken and exposed. On the whole, much of the coupling should tend to be irreversible, the stone should shrink and become stronger and less susceptible to moisture change. For example, sorption of nitrocotton may be reduced to two-thirds of its original value by this means."

McBain and Ferguson's hysteresis cycles for Gatton stone were started with material already containing a certain amount of water. The curves are not extended to the origin of zero pressure and zero moisture content. It is to be inferred from their proposed explanation that a certain amount of water was irreversibly coupled to the adsorbent, although this was not tested by continuing desorption to zero pressures. In the form given, their hypothesis is not adequate for the moisture sorption by cellulose esters, because there is no permanent or irreversible coupling of absorbed water, and no permanent decrease of the amount of water adsorbed, with attending complete disappearance of hysteresis.

We do not feel that a complete explanation of the hysteresis phenomena is yet available. A modification of McBain and Ferguson's hypothesis might be attempted in terms of relative exposure and burying of active, OH groups, hence of change of the wetting power, which is consistent with the first explanation in terms of contact angle. This would involve a certain amount of superficial reorientation of the molecular units, and this is supported by observations of A. H. Nietz[22] on the change of work of adhesion of alcohol and water to cellulose acetate on alternate treatment with more and less polar liquids. The problem requires fuller investigation with cellulose esters (nitrates, acetates and ethers) in which all OH groups have been, as far as possible, removed by esterification. It has been pointed out that cellulose triacetate, should, on chemical grounds, show probably no higher absorption than cellobiose octacetate. Again, Will's formula for moisture absorption by cellulose acetate would make the absorption for a completely nitrated material at 14.2% N practically zero.

We propose therefore to examine the sorption phenomena of such completely esterified materials. It should then be possible to determine whether the sorption and hysteresis with the less de-hydroxylated materials cannot be explained in terms of surface reorientations of atom groups of the adsorbent, with attending changes in gel structure.

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[3] *Cf.* Deluc: Phil. Trans. Roy. Soc., 81, 1389 (1791); P. von Schröder, Z. physik. Chem., 45, 109 (1903).

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[6] *Cf.* for example, Urquhart and Williams: J. Text. Inst., 15, T138, 443, 559 (1924); 16, T155, (1925); 18, T55 (1927).

[7] Differences in reactivity cannot be regarded in heterogeneous reactions as evidence for such changes. The only significant difference at present is the observation of H. T. Clarke and C. J. Malm, (J. Amer. Chem. Soc., 51, 274 (1929)) that normal cellulose boiled with fatty acids fixes about 1 molecule acid per 24 C-atoms; hydrate celluloses, (by mercerization or regeneration) fix about 1 molecule per 6 C-atoms.

[8] *Cf.* R. O. Herzog: J. Phys. Chem., 30, 457 (1926).

[9] R. O. Herzog: loc. cit.

[10] K. H. Meyer and H. Mark: Ber., 61, 593 (1928).

[11] Very possibly involving a more spiral ordering.

[12] Loc. cit.

[13] In a later paper (Mark and Meyer: Z. physik. Chem., B2, 115 (1929)) modified to slightly monoclinic.

[14] R. O. Herzog: Ber., 60, 600 (1927).

[15] *Cf.* J. Katz, in K. Hess "Die Chemie der Zellulose," (1928).

[16] For the distinction between intra-micellar and inter-micellar swelling, see J. Katz: Kolloidchem. Beihefte, 9, 57 (1916).

[17] *Cf.* J. J. Trillat, and R. Scelles: Revue des Colloides., 6, 177 (1928).

[18] Loc. cit.

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[20] It is not always understood that the reaction is heterogeneous in both cases.

[21] *Cf.* Meyer and Mark: loc. cit.

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[26] Very probably *orientation* in smectic form is continued in the solutions—all that is necessary is free movement to form plane layer, *i.e.*, about the axes.

[27] Mitt. Schiess. u. Sprengstoff., Neu Babelsburg, 1904.

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April 8, 1929

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A STUDY OF THE ACTION OF LIGHT OF DIFFERENT WAVE-LENGTHS ON NITROCELLULOSE*

BY H. B. DEVORE, A. H. PFUND AND V. COFMAN

Berthelot and Gaudechon[1] have shown that nitrocellulose is decomposed by ultra-violet light with evolution of CO_2, CO, N_2, and N_2O. On the basis of their work, Guilbaud[2] constructed an apparatus for the measurement of these decomposition products. Since then very little work on the photochemical decomposition of nitrocellulose has been reported.

The action of sunlight or ultra-violet light on an unpigmented nitrocellulose film is accompanied by a variety of phenomena in addition to the gaseous decomposition. The film becomes acid, its brittleness increases, its tensile strength decreases, and after prolonged exposure the film becomes yellow. The viscosity of a solution prepared by redissolving an irradiated film is lower than that of the solution from which the film was cast.

The work described in this paper was undertaken with the purpose of determining the spectral region responsible for the decomposition, and of finding some convenient method whereby the decomposition by light of different wave-lengths can be measured.

Experimental

The nitrocellulose used in this work was a low viscosity nitrocotton containing 12.4% nitrogen. The films were formed with a 10% solution[3] of this nitrocellulose in a mixture of 80% ethyl acetate with 20% ethyl alcohol.

The source of ultra-violet radiation was a Cooper-Hewitt vertical Uviarc, a mercury arc in quartz. This was operated with 168 volts across the tube and with a current of 3.7 amp.

Thin Film

Our first experiments made use of the decomposition of the film itself. Very thin films of nitrocellulose were made by spreading a small quantity of solution on the surface of water or mercury and removing the film formed on a wire ring. The thickness of these films was of the order of magnitude of 0.001 mm., and when properly made they showed a fairly uniform interference color over the entire surface. Films of this type, exposed to the quartz mercury arc, were gradually decomposed by the light with formation of gas. This decomposition was accompanied by a progressive change in

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* Contribution No. 15 from the Experimental Station of E. I. duPont de Nemours and Company.

[1] Compt. rend., **154**, 201 (1912).

[2] Compt. rend., **161**, 212 (1915).

[3] The words *solution* and *solubility* are used here for the sake of simplicity. Nitrocellulose forms colloidal dispersions with organic solvents.

the thickness of the film, and a corresponding variation in the interference color shown by the film. In order to determine the spectral region which is responsible for this decomposition, a film showing a uniform blue interference color was placed in the focal plane of a Gaertner quartz spectrograph and exposed to the mercury arc for 60 hours. The result was a number of yellow lines (interference color) on the film, corresponding to the portion of the mercury arc spectrum extending from 260 mμ to 190 mμ. This showed the very powerful action of the far ultra-violet but did not, within a reasonable time of exposure, indicate any action by the near ultra-violet which is present in sunlight.

Indicator Method

Another method which was used for the measurement of film decomposition was based on the fact that nitrocellulose films increase in acidity when exposed to the action of ultra-violet light. The apparent pH of a 10% solution of nitrocellulose in ethyl acetate is approximately 4, as shown by indicators. The units in which the acidity is expressed are described as apparent pH, since the pH of a non-aqueous solution does not necessarily have the same meaning as for an aqueous solution. Of the number of indicators having pH ranges around 4, bromphenol blue (tetrabromphenol sulfon phthalein) was found to be the most satisfactory as to sensitivity to acidity developed in films. The films were made by spreading a 10% solution of nitrocellulose, containing 0.01% of bromphenol blue, on a glass plate by means of a "doctor" knife. These films were of a deep blue color; on exposure to the mercury arc, the color changed to yellow, as a consequence of the reduction in pH of the film, produced by the action of the radiation on the nitrocellulose. Films of this type were placed in the quartz spectrograph and exposed for one or two days. A yellow mercury arc spectrum on a blue field was obtained. The intensity of action of the various rays was represented roughly by the degree of color change in the lines formed. This spectrum extended approximately from 600 mμ to 230 mμ.

Attempts were made to measure the relative effects produced by lines of different wave-lengths in terms of the different intensities of color change. For this purpose measurements on the film were made with a microphotometer. However, since the thermopile on this instrument was equally sensitive to yellow and to blue light, it did not distinguish between the different colored lines. A further experiment was made by printing the nitrocellulose films in yellow light on photographic plates. The yellow lines printed black while the blue field absorbed most of the yellow light and produced very little effect on the plate. The spectrum was then represented as black lines on a light field. These plates were measured with a microphotometer and the result was slightly more successful than measurements on the nitrocellulose films. A typical microphotometer record is shown in Fig. 1.

One objection to this method lies in the fact that the color change in the indicator is relatively limited. When the acidity reaches pH 3.4, the color of the bromphenol blue turns deep yellow. Lowering of the pH beyond this point does not produce any further change. This limitation in the color change leads to over-exposure and consequently to an under-estimation of the activity of the stronger lines, when an exposure sufficiently long to show the weaker lines is given. Another objection to the microphotometer method of evaluating the relative activities of different parts of the spectrum lies the fact that exposure to ultra-violet light changes the absorption characteristics of the film. When the color of the film changes, the absorption for the incident light is altered and the rays of different wave-lengths are acting under different conditions, depending on the alteration produced by each in its particular part of the film. In addition to the modification in absorption of the film as a result of color change in the dye, the absorption characteristics of the nitrocellulose itself are altered by exposure.

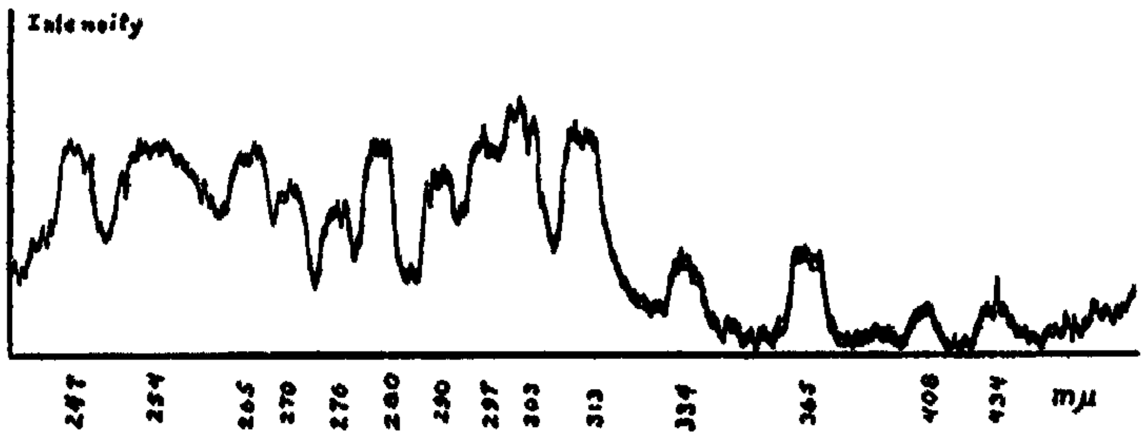

FIG. 1
Microphotometer Record of Spectrum on a Dyed Film

Threshold Method

In order to obviate the two sources of error introduced by the narrow range of the indicator and the changes in the absorption characteristics of the film, a threshold value—the time of exposure required for initial appearance—was measured for each spectral line. The activities of the various wave-lengths of light are taken as inversely proportional to these values. For the determination of the threshold values, a series of exposures of increasing duration was made on a film and the time required for each line to appear was found by inspection. By this method a strong maximum of activity was found at about 313 mμ.

To convert the activity of each wave-length of light into relative effectiveness two things are needed: the relative energies of the different mercury lines as transmitted by the quartz spectrograph used in this work, and the coefficient of absorption of the film for each wave-length of the mercury spectrum.

For the purpose of measuring the energy distribution in the spectrum, the quartz spectrograph was converted into a simple form of monochromator by replacing the plate holder by a moveable slit. A compensated vacuum thermopile was placed before the collimating slit and the mercury arc located beyond the moveable slit. The arrangement is shown in the diagram in Fig. 2. The moveable slit was adjusted for each of the prominent lines in the mercury arc spectrum and the energy of the line measured by the thermopile in conjunction with a Leeds and Northrup high sensitivity galvanometer. The ultra-violet absorption of the films was measured by an ultra-violet spectrophotometer consisting of an arrangement very similar to that described for the energy measurements. To find the amount of light of any given wave-length transmitted by the film, the intensity of that wave-length transmitted by the monochromator was first measured. The film was then inserted between the arc and the monochromator and the intensity again measured. The ratio of the two intensities gives the amount of light transmitted by the film in each case, and these values subtracted from unity give the amount of light absorbed by the film.

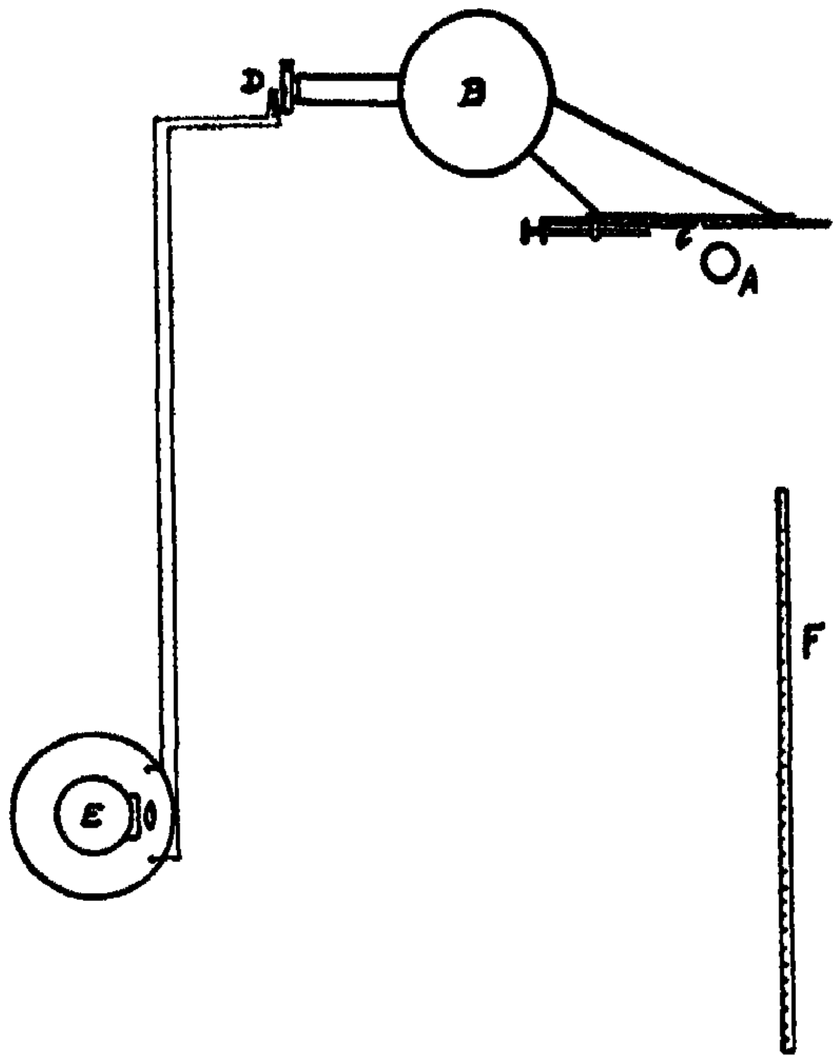

Fig. 2

Arrangement of Apparatus for Energy Measurements

A—Mercury Arc
B—Quartz Spectrograph
C—Moveable Slit
D—Compensated Thermopile
E—Galvanometer
F—Scale

In order to determine the degree of decomposition of nitro-cellulose with the use of a film containing a dye, it is necessary to be certain that the light has no action on the dye, and that there is no reaction of the dye with the nitrocellulose nor any reaction in which the dye functions as a catalyst for the decomposition of the nitrocellulose. Accordingly, clear films of nitrocellulose were given exposures of one day in the quartz spectrograph, and afterwards dyed with bromphenol blue. The unexposed parts of the film were stained blue, but in the exposed portions, the indicator changed its color as it was absorbed. In this way a film showing yellow spectral lines on a blue field was obtained. This method of "development" clearly showed the production of acidity and obviated the chance of any side reactions due to the presence of bromphenol blue in the film. In the process finally worked out for this development, the film was painted with an alcoholic solution of the dye. The developed films showed lines from 190 mμ to 400 mμ. The strongest yellow color appeared to be at about 260 mμ.

Efficiencies of the Different Wave-Lengths

In the series of graded exposures the activity of light of any wave-length is inversely proportional to the time required for the first appearance of its line. Also, the time required for its appearance being constant, the activity is inversely proportional to the energy of that particular wave-length and to the absorption coefficient of the film for light of that wave-length. The relative effectiveness of the various lines may then be represented by the reciprocal of the product of time of appearance by energy and by the absorption coefficient. In Fig. 3 the relative effectiveness or the efficiency for each line is plotted against its wave-length. The experimental error is rather high because of the difficulty of determining with any accuracy the time required for a line to just make its appearance. There is, however, a sharp peak in the curve indicating a strong maximum of decomposition per unit energy in the region represented by the line at 313mμ.

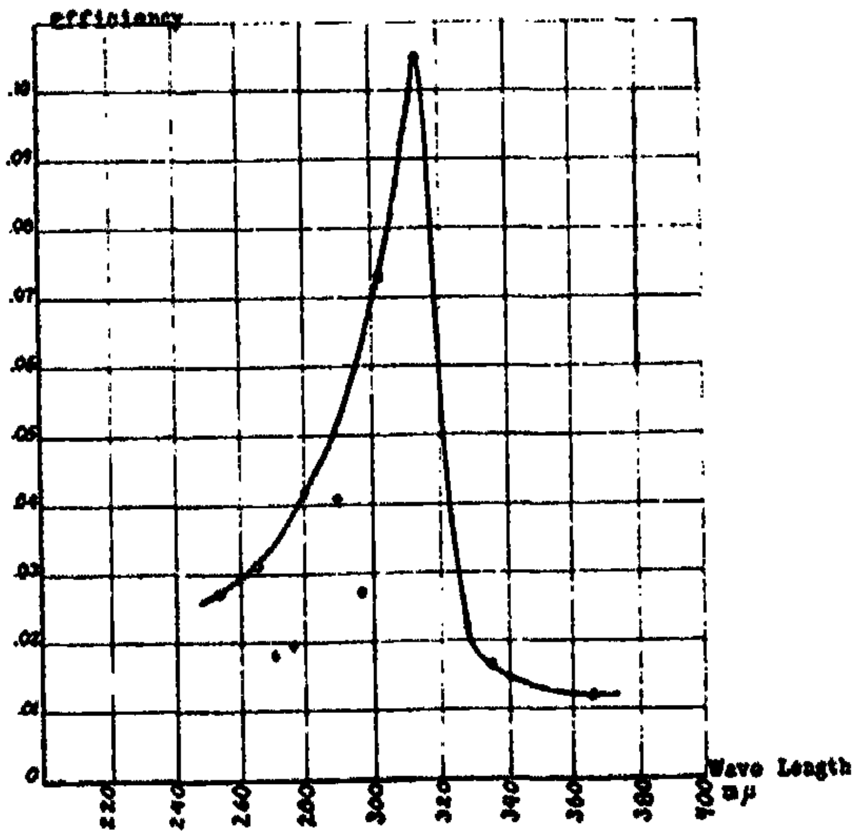

Fig. 3
Energy Efficiencies

In Fig. 4 quantum efficiencies are plotted against wave-lengths. Since the quantum efficiency of any wave-length is inversely proportional to the number of quanta of that wave-length present, the relative efficiencies of the various wave-lengths are found by taking the reciprocal of the product of the time of appearance of the line by the absorption coefficient for the line and by the number of quanta present. These relative efficiencies in empirical units are obtained by dividing the relative energy efficiencies by the wave-lengths of the lines.

The wave-lengths of the light showing the maximum activity in each of the methods used are given below.

Thin Films	250 mμ
Clear Films developed with bromphenol blue solution	260 mμ
Dyed Films	313 mμ

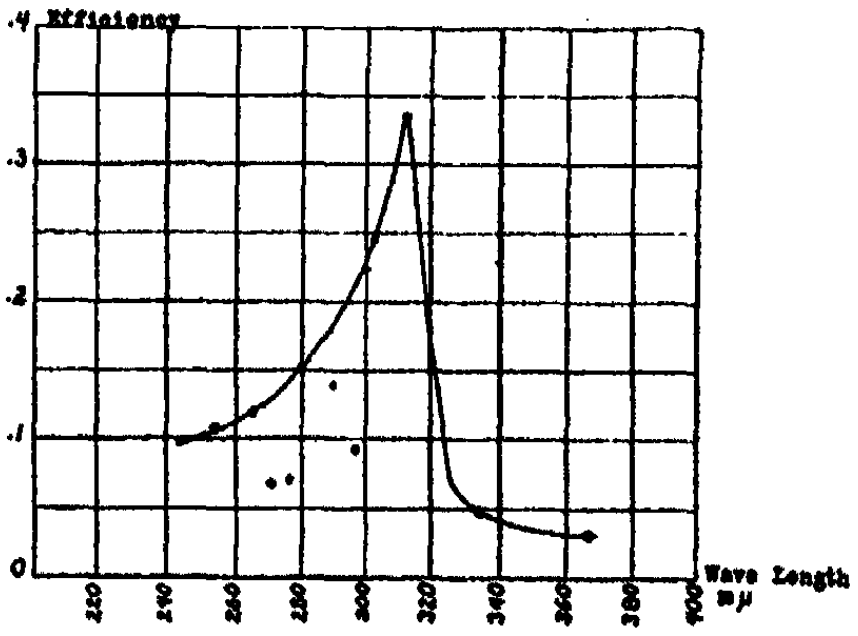

Fig. 4
Quautum Efficiencies

The difference in these values is readily explainable if one considers the absorption of ultra-violet light by the nitrocellulose. Nitrocellulose films of the thickness used (0.05 mm.) are almost completely opaque to wave-lengths shorter than 260 mμ, so that nearly all of the energy of the light having wave-lengths 265 mμ and below is absorbed very close to the surface. These lines have a very powerful action which is, however, confined to the surface of the film. They are particularly effective in very thin films where nearly the entire energy of the lines 254 mμ, and below, is absorbed and causes decomposition. This surface effect is also conspicuous in the films which were developed by painting with bromphenol blue, where the depth of penetration of the dye was very small. The lines produced by light of short wave-lengths, which had acted on the surface only, were brought out and were not obscured by a relatively large thickness of dyed film.

The light of wave-lengths 300mμ, and above, was very much less absorbed by the film so that the decomposition of nitrocellulose produced by this light was distributed throughout the film. Consequently, the entire thickness of the film was changed in color where the longer wave-lengths acted upon it and there was no masking action of unaffected film.

Other Effects

Films of nitrocelluose containing diphenylamine developed a yellow-brown color on exposure to the mercury arc. This reaction indicated the presence of free nitrous acid in the film. This is in agreement with the discoloration of malachite green in celluloid described by Rayleigh[1] as has been pointed out by the authors.[2]

Two other phenomena of considerable interest have been observed. The first is the change in solubility produced by ultra-violet light. This was shown by an increased ease of penetration of solvent into the film after exposure. Clear films of nitrocellulose were exposed in the quartz spectrograph and then placed in a mixture of acetone and water. Since nitro-cellulose is insoluble in water, a precipitate of nitrocellulose in the film was formed as rapidly as its absorption for acetone permitted the mixture to penetrate the film. This precipitate gave a cloudy white appearance to the film (blushing). The exposure of the film in the spectrograph increased its solubility to such an extent that the lines of the mercury arc turned white before there was any apparent action of the solvent mixture on the unexposed film. In this way was obtained a mercury arc spectrum in the form of white lines on a clear film.


Fig. 5
Cracking of Film at the
λ 254 mμ Line

The other very striking effect is the production of brittleness in the film by light of about 254 mμ wave length. A film of nitrocellulose which had been exposed in the quartz spectrograph for a week was bent double along the length of the exposed strip. A microscopic examination showed a great number of minute cracks at that part of the strip which had been exposed to the 254 mμ ray. This brittleness was found again in another film which had been exposed for a week in the quartz spectrograph and then placed in an acetone-water mixture to show "blushing." Every line showed a uniform white appearance except the 254 mμ line which developed a great number of cracks. Fig. 5 shows a photograph of this line considerably enlarged.

Summary

The action of light on nitrocellulose as a function of wave-length has been investigated spectrographically by means of the decomposition of very thin films (0.001 mm.) and of thicker films containing acidity indicators.

(1) Thickness of thin films is reduced by λ190-260 mμ.

(2) Acidity is increased by λ230-600 mμ with a strong maximum around 313 mμ.

(3) The imbibing power of films is increased by the same spectral region.

(4) Brittleness is produced by wave-lengths around λ254 mμ much more rapidly than by the longer wave-lengths.

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[1] Nature, **122**, 645 (1928).

[2] Nature, **123**, 87 (1928).

STOICHIOMETRIC RELATIONS IN HYDROCHLORIC ACID-GELATIN SYSTEMS FROM VISCOSITY MEASUREMENTS

BY EGBERT K. BACON

The stoichiometric nature of the reaction between gelatin and HCl as indicated from viscosity measurements in these systems is shown in the work presented here. Such relations have been disregarded or overlooked by many. Kruyt[1] and his co-workers consider that the stoichiometric phases of protein-acid systems are of relative non-importance if not non-existent, the mechanism of behavior of these lyophilic colloids being governed by electrokinetic phenomena the same as that of lyophobic colloids. Many others favor the purely colloidal point of view. Examples of recent work are given in papers by Ghosh[2] and Fanselow[3].

Recognition of the chemical relations existing between protein and acid or base is generally accepted among others.[4] They consider that the behavior of lyophilic colloids such as those of the proteins is determined largely by the chemical groups which constitute the molecule. Thus in the presence of acids and bases ionizable salts of more or less definite composition are formed and such solutions owe their properties to the presence of these ions.

The importance of this latter point of view has been shown in measurements of diffusion potentials in concentration cells containing HCl and gelatin.[5] The plotted values for the diffusion potentials with change in concentration of acid and gelatin indicated the formation of a highly ionized gelatin salt and gave the equivalent weight[6] of gelatin as close to 1090.

Further work[7] demonstrated the importance of defining gelatin—HCl solutions in terms of free acid, pure gelatin, and gelatin salt.

The present investigation is an attempt to apply the ideas outlined in these previous papers to viscosity measurements on similar systems. The results show the same stoichiometric relations that were indicated in that work.

Many investigations have been carried out on the measurement of viscosity of gelatin solutions.[8] Practically all of this has been considered from

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[1] H. R. Kruyt: "Colloids," (1927). Translated by H. S. van Klooster.

[2] Ghosh: J. Chem. Soc., 130, 711 (1928).

[3] Fanselow: Colloid Symposium Monograph, 6 (1928).

[4] T. B. Robertson: "The Physical Chemistry of the Proteins," (1920); J. Loeb: "Proteins and the Theory of Colloidal Behavior" (1922), (1924); F. Bottazzi: "Colloid Chemistry." Ed. by Jerome Alexander, 2, (1928).

[5] Ferguson and Bacon: J. Am. Chem. Soc., 49, 1921 (1927).

[6] Recent work of Hitchcock (J. Gen. Physiol., 12, 495, (1929)) confirms this value. Inferring isoelectric gelatin to be at a pH of 5.0 instead of 4.7 he finds that 9.4×10^{-4} equivalents of H^+ ion in .10 M HCl combines with 1 g. of gelatin. An equivalent weight of 1090 corresponds to 9.1×10^{-4} equivalents of H^+ ion calculated on the same basis.

[7] Bacon and Ferguson: J. Am. Chem. Soc., 49, 1934 (1927).

[8] Loeb: "Proteins and the Theory of Colloidal Behavior" (1924); Davis, Oakes and Browne: J. Am. Chem. Soc., 43, 1526 (1921); Bogue: 43, 1764 (1921); Freundlich and Neurkircher, Kolloid-Z., 38, 181 (1926); Loebel: J. Phys. Chem., 23, 763 (1928) and many others.

the point of view of the pH, viscosity curves for gelatin and acid or base. Such curves reveal little except that the viscosity is a function of the pH and that solutions of gelatin of the same concentration, prepared in the same way, and of the same pH have the same viscosity. Thus many workers who have adopted the view of the existence of compound formation between gelatin and acid or base have failed to consider in their work the influence of the very thing which they believe to be present. Davis, Oakes and Browne say that "the maximum in the curve (viscosity, pH curve) at pH 3 to 3.5 is unaccounted for except on the assumption of the formation of a compound at this point. Data included in a paper in the course of preparation supports this view." As far as the writer is aware further support of this statement has failed to appear in any of their subsequent papers.

Experimental

Viscosity measurements were made with the Ostwald type viscosimeter.

The temperature for all determinations was 40°C. This temperature was maintained by an electrically controlled thermostat regulated to 40°C ± .05.

The gelatin was a pure, ash-free, calfskin gelatin, a standard product of the Eastman Kodak Company. No attempt was made to subject this to any special treatment. The moisture content was found to be about 14.5%. This was determined by heating to constant weight at 110°C. and was applied as a correction to all weighings.

The hydrochloric acid was of C.P. quality, standardized as 0.10 M by analysis as AgCl.

The results are indicated in the form of the viscosity ratio

$$\text{Vis. ratio} = \frac{\text{Time of flow of gelatin solution at } 40^\circ\text{C.}}{\text{Time of flow for water at } 25^\circ\text{C.}}$$

This is quite permissible since it has been shown[1] that solutions of gelatin or gelatin and HCl of varying concentrations show little change in density.

Furthermore the ageing effects that are always apparent in viscosity measurements on gelatin systems vitiate any real meaning for absolute values.

Measurements were made on a series of three different concentrations of originally uncombined gelatin with varying concentration of .10M HCl. One series had the concentration of .545 g. of dry gelatin per 100 cc. of solution, the other 1.09 g. and the third 2.18 grams. Since it has been determined that the equivalent weight of gelatin is approximately 1090, the first series may be designated as a .05 N solution of gelatin, the second as .10 N and the third as .20 N.

It is well known that the viscosity of gelatin solutions varies with the manner in which the solutions are made and that such solutions show subsequent variations with time, the extent and nature of the variations depending upon conditions. For this reason a uniform procedure was used in making up all solutions.

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[1] Davis and Oakes: J. Am. Chem. Soc., 44, 464 (1922).

The gelatin was weighed out to the nearest milligram, transferred to a small beaker, about 30 cc. of boiled distilled water were added and the solution effected by stirring and heating on an electric hot plate until the temperature reached 70°C. With the concentrations of gelatin used, this process consumed approximately five minutes. The solution was then transferred to a 100 cc. volumetric flask, cooled to about 40°–50°C. and .10 M HCl run in from a burette. It was next diluted with water, thoroughly shaken and filtered twice. A portion was transferred to a small glass-stoppered flask and placed in the thermostat for 10 minutes. Five ccs. were then introduced into the viscosimeter by means of a pipette and the time of flow measured after 10 minutes. In all cases the first measurement of flow was made at approximately one hour after the gelatin had first started to dissolve. At least six measurements were made with each solution at five minute intervals. The ageing effect during this time was usually very small. Each determination was made with a freshly prepared gelatin solution and duplicate determinations were made at various times thruout the course of the work to prove that all results are definitely reproducible.

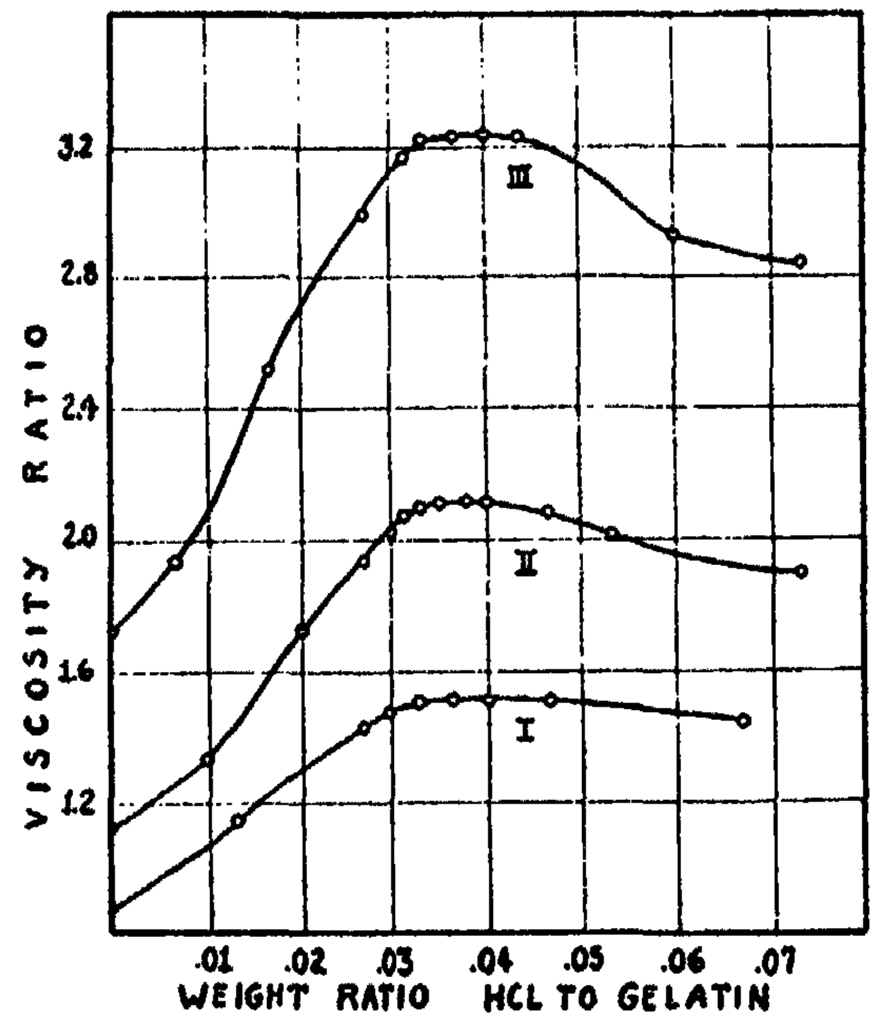

Fig. 1

Viscosity changes of gelatin-HCl solutions at 40°C with increasing concentration of HCl.

Curve I—0.545 g. gelatin per 100 cc solution
II—1.09 g. gelatin
III—2.18 g. gelatin

Fig. 1 shows the results of these measurements with the three series of solutions. The viscosity ratio is plotted against the ratio of grams of acid present in 100 cc. of solution to grams of gelatin present in the same volume. In each of the three curves the viscosity rises to a maximum value as the concentration of acid becomes greater. The maximum point in each curve occurs at the same value for the ratio of HCl to gelatin. This value is approximately 0.034 and represents the ratio between an equivalent of HCl, 36.5 g., and an equivalent of gelatin, 1090 g. Beyond this point further increase in acid concentration produces at first slight change in the viscosity which is then followed by a gradual and definite decrease. The maximum is sharply defined in each case and consists in a rather sharp break in each curve. With the lowest concentration of gelatin (0.545 g.) the break in the curve occurs when .5 milli-equivalents of HCl is present. With gelatin concentration twice as great (1.09 g.) the break occurs at an acid concentration of 1 milli-equivalent and with the gelatin concentration four times as great (2.18 g.) as in the first the break occurs at 2 milli-equivalents of acid. Thus the critical points on the three curves correspond to a definite stoichiometric relationship between the amount of gelatin present and the amount of acid added. Furthermore each of these points represent a condition where acid and gelatin have combined in equivalent proportions, considering the equivalent weight of gelatin to be about 1090.

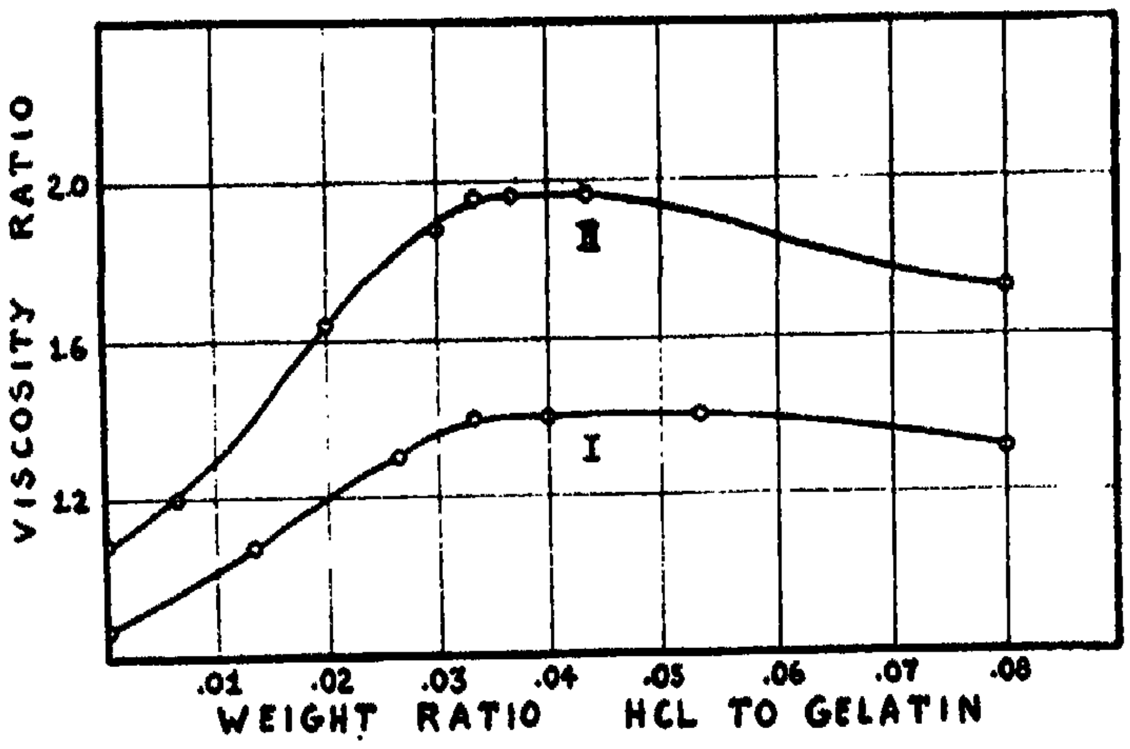

Fig. 2

Viscosity changes of gelatin-HCl solutions at 40°C with increasing concentration of HCl. Gelatin solution heated one hour at 70°C before addition of HCl.
Curve I—.545 g. gelatin. Curve II—1.09 g. gelatin.

The influence of the method of preparing the solutions upon the combining ratios for gelatin and acid was next investigated. Viscosity measurements for the two lower concentrations of gelatin, 0.05 N and 0.10 N, in which the solutions were prepared in a different way, were carried out as follows.

The required amount of gelatin was weighed out, and dissolved as before. The solution was then transferred to a 100 cc. volumetric flask and maintained at a temperature of 70°C. for a period of one hour. It was cooled slightly, acid added and diluted to 100 cc. The viscosity was then determined in the manner described previously.

Results obtained from this treatment are shown in Fig. 2. With both concentrations of gelatin the viscosity of uncombined gelatin was lowered but slightly by the prolonged heating. After the addition of acid, however, the viscosity in all cases was decidedly lower. The general shape of the curves are the same as in Fig. 1 and the breaks in both curves occur at exactly the same ratio of acid to gelatin. This indicates that the combining capacity of gelatin for HCl has not been changed.[1]

The pH of the solutions used in both treatments was determined colorimetrically and checked against the hydrogen electrode. The three concentrations of the original gelatin without the presence of acid were at pH 4.7 and the three concentrations of pure gelatin chloride, as represented by the maximum in each curve, at approximately pH 3.0.

Discussion

The curves of Figs. 1 and 2 indicate a definite stoichiometric relationship between the concentration of gelatin and the concentration of acid which is independent of the method of effecting solution and is reproducible in all cases. This relationship suggests definite compound formation between the gelatin and the HCl. These conclusions are contrary to the opinion of Kruyt[2] who says: "One would err, however, in assuming that two 1 per cent solutions of gelatin were stoichiometrically on a par."

If the process of prolonged heating changed the degree of dispersion[3] and if the capacity for combination between gelatin and acid depended upon particle size, the reaction taking place at the surface of polymolecular units, then we would expect to obtain a different combining ratio. The experiments show, however, that this is not the case. If a gelatin solution consists principally of associated molecules and association is decreased by prolonged heating, it appears that the active groups in the molecule retain their same capacity for combination whether they are associated or not. Thus if a gelatin micelle is pictured as an aggregate, a chain or a netlike structure, the reactive groups in each molecule may be capable of combination with HCl whether associated in this form or independent of each other. Such a picture does not exclude the possibility of the presence of micelles under certain conditions but it does indicate the definite capacity for reaction of the single molecules. The micelles are not the reacting units themselves but rather the

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[1] Independence of temperature of effecting solution is shown in pH, viscosity curves for gelatin-HCl solutions by Loebel: J. Phys. Chem., 23, 763 (1928).

[2] "Colloid Chemistry," 198 (1927).

[3] The work of M. Frankel (Kolloid-Z., 45, 355 (1928)) suggests that ageing effects in gelatin solutions at different temperatures is due to a dissociation of particles, the chemical properties, however, remaining unaffected.

individual molecules. Some such idea as this seems necessary to reconcile the colloidal behavior of gelatin solutions with that of their purely chemical behavior.

The viscosity of gelatin solutions alone or in the presence of acid is probably due to a number of factors. Theories such as those of Dhar[1] which suggests a varying degree of hydration with charged and uncharged particles and the lyotropic effect of ions of the added electrolyte or the "electroviscous" effect suggested by Kruyt which is also determined by adsorption, hydration and lyotropic effects, seem inadequate as these theories do not take into consideration gelatin salt formation and regard stoichiometric relations as incidental in the system.

Pauli's hydration theory[2] which does consider protein salt formation might be questioned and it seems certain to the writer that Loeb's explanation on the basis of the Donnan equilibrium is not plausible.[3]

Robertson has given an interesting account of the origin of viscosity in protein solutions.[4]

He considers the protein molecule to be a multipole of high electrical moment. The consequence of this is, that in a solution of uncombined gelatin there is a definite orientation of molecules in aggregates or netlike structure. Thus, these attractive forces impose a resistance to flow which gives rise to the viscosity. When acid or base is added to such a gelatin solution, the magnitude of the electrostatic forces increase and as a result the viscosity becomes greater. The maximum effect would thus be obtained when all the gelatin was present in the combined state as gelatin ions. This would correspond to the maximum point and break on the curves which are shown here. The effect of presence of excess ions of electrolyte would tend to nullify the electrostatic repulsion of the protein ions with corresponding decrease in viscosity.

Such a type of explanation seems compatible with the facts which have been presented here, since it takes into account the stoichiometric relations involved in the systems and the definite formation of gelatin salt. These facts cannot be overlooked in any theory of viscosity.

Summary

1. Viscosity measurements at 40°C. have been made on systems of ash free gelatin and hydrochloric acid.

2. Plotted values for the viscosity ratio with changing concentrations of gelatin and hydrochloric acid indicate a stoichiometric relation between gelatin and acid. This supports the view that definite salt formation results from the interaction of gelatin and HCl and that the equivalent weight of gelatin is about 1090.

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[1] Dhar: J. Phys. Chem., 29, 1556 (1925).

[2] W. Pauli: "The Colloid Chemistry of the Proteins" (1922).

[3] Calculations of diffusion potentials in gelatin-HCl systems as determined in previous work appear to deny the existence of a Donnan membrane potential. These calculations remain as yet unpublished.

[4] T. B. Robertson: Colloid Chemistry, Ed. by Jerome Alexander, 2 (1928).

3. Structural changes in gelatin solutions as evidenced by viscosity changes due to ageing, method of preparation, and temperature are independent of the combining ratio for gelatin with HCl. From this it appears that the reactive units are the chemical groups in the molecules themselves rather than aggregates or micelles.

4. Theories of viscosity which consider only adsorption, hydration and lyotropic effects appear to be inadequate explanations for the results obtained here.

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A NEW THERMOREGULATOR: IMPROVEMENTS

BY S. C. COLLINS

The thermoregulator, described in the Journal of Physical Chemistry, **31**, 1097-1098 (1927) depends for its action upon the differential expansion of air and the saturated vapor of ether or other liquid. If the sensitive member of the regulator should be accidentally overturned, it is completely ruined because of the mixing of the air and ether vapor. In the improved form, however, the design is such that mixing of the fluids is impossible.

In the diagram, B represents the sensitive member. It is partly filled with mercury, the remaining space in one bulb containing air, that in the other containing a volatile liquid and its vapor. The two bulbs are connected by a narrow tube. The mechanism is balanced at a point slightly above its center of mass. With a very small rise in temperature, the vapor pressure of the liquid increases enough more rapidly than the air pressure in the other end to force some of the mercury from the bulb on the right into the one on the left. This causes a change in the position of the tube, thereby breaking the heating circuit at S. By adjusting the tension on the spring C, the operating temperature can be varied at will.

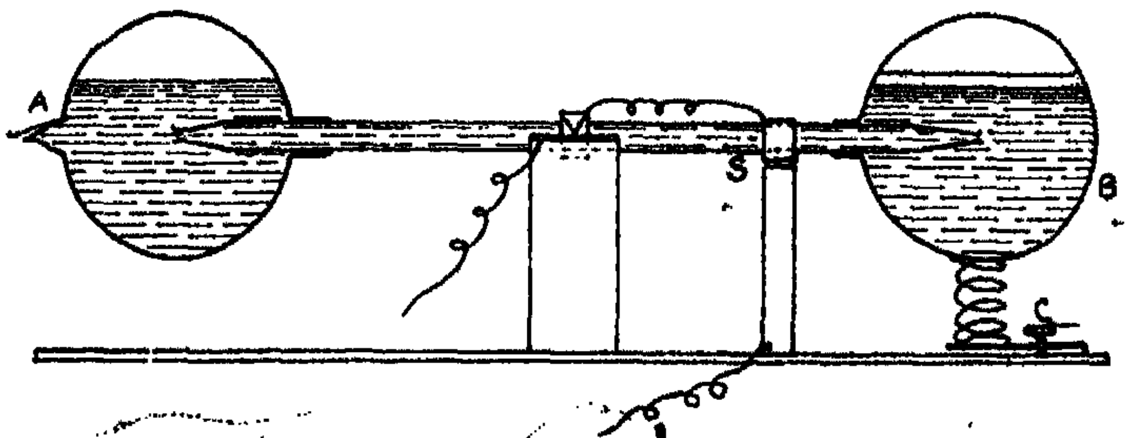

FIG. 1

The openings in the ends of the connecting tube are at the center of their respective bulbs. Since each bulb is always somewhat more than half full of mercury, it is obviously impossible for either air or ether to enter the tube and pass to the other bulb, no matter in what position the tube may be held.

The instrument now being used in this laboratory is made of glass, though steel would perhaps be more desirable. The connecting tube is 5 mm in diameter and 15 cm long. The bulbs were blown from tubing just large enough to slip over the ends of the connecting tube and were sealed at the proper position. An opening was left in one bulb at A. After filling, the opening was sealed in the flame.

If it is desired, this regulator could be used in a water-bath just as the one previously described.

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NEW BOOKS

Enzyme Actions and Properties. *By Ernest Waldschmidt-Leitz. Translated by Robert P. Walton.* 23 × 15 cm; *pp. xviii* + 255. *New York: John Wiley and Sons, 1929. Price: $4.00.* In the preface the translator says: "The phenomena of enzyme actions represent a signally prominent aspect of organic chemistry. The mechanisms of those chemical transformations taking place in the life processes of plants and animals are effected principally by the action of enzymes. In fact, it has been whimsically said that life is just one enzyme reaction after another. Certain it is that the significance of enzyme transformations in biological processes is to be regarded as of the first magnitude. Beyond the purely biochemical aspects, enzyme reagents have been used to advantage in elucidating the constitution of high molecular organic compounds and also in the preparation of easily alterable, organic substances. Among the purely utilitarian phases of enzyme study may be mentioned the application of enzymes to medical diagnosis, to the control of diseases and to the performance of numerous industrial operations. These latter phases offer a particularly attractive incentive to the further application of enzymic principles.

"The material within this volume constitutes a general treatment of enzyme action and properties as interpreted principally from the viewpoint of the Willstätter school. Prof. E. Waldschmidt-Leitz, the active associate of R. Willstätter, has given a condensed description of the most important principles of enzyme chemistry and of the special characteristics the most prominent enzymes. The work has not been attempted as an exhaustive compendium of enzyme literature but rather as a concise presentation of the most fundamental principles and best accepted characteristics of enzyme action.

"The original German text has been considerably extended, although the additions have been principally from the viewpoint of the Willstätter school. The purpose of the modifications has been primarily to bring the context of the volume up to the present date rather than to impose any particular viewpoint of the translator. This revision and extension has been carried out with the cooperation of the author and warmest thanks are due him for his careful consideration in this work."

The chapters are entitled: development of the ferment concept; enzymes as colloids; enzymes as electrolytes; enzymic kinetics; enzymic reaction systems; enzymic specificity; detailed procedures in preparative enzyme chemistry; esterases; proteases and peptidases; aminoacylases; carbohydrases; catalases; peroxydases; oxydases; fermentation enzymes.

"Ezymes may be defined as definite material catalyzers of organic nature with specific powers of reaction, formed indeed by living cells, but independent of the presence of the latter in their operation, p. 3. Willstätter considers that the enzymes are composed of a colloidal bearer and a specific active group, which enables them to be bound to the substrate, and the composition of which at the same time conditions the colloidal nature of the entire complex," p. 6.

"By means of a guiding principle that all substances which are absorbed by the electronegative adsorbent kaolin are to be regarded as bases, and that all those adsorbed by the electropositive alumina are to be regarded as acid, they investigated the chemical nature of a number of enzymes. The methods were not quantitative, but merely a sort of approximation. Invertase, which is adsorbed by alumina in every case, but on the contrary not in the slightest adsorbed by kaolin, exhibited according to this method the character of an acid, which is in full agreement with its migration behavior. Saliva amylase and trypsin, which are taken up by alumina as well as by kaolin in every reaction, were regarded on the other hand as amphoteric substances.

"These observations, which were accentuated in crude enzyme solutions, do not hold good for the enzymes themselves as proven by Willstätter, but only for their aggregates with concomitant substances. Thus it has been demonstrated that invertase is adsorbed from purer solutions by kaolin, and also even from crude yeast autolysates under certain conditions; hence it possesses basic as well as acid properties. Trypsin, after an imperfect separation, is no longer taken up at all by alumina, but, on the other hand, is taken up quantitatively by kaolin; its basic nature is thus demonstrated. Finally, animal amylase is less and less adsorbed by both basic and acid substances as its degree of purity increases. Hence the true adsorption behavior of enzymes is only recognizable in the higher degrees of purity," p. 19.

"The investigations described in the foregoing paragraphs of the chapter have proved that in a series of cases, especially for the action of carbohydrate-splitting enzymes, the course of enzymic reactions can be expressed with fair accuracy on the basis of the mass action law, and further, that the total concentration of the substrate is responsible for the reaction velocities and not merely a definite adsorbed fraction of the substrate. The equilibrium between the enzyme and the substrate is determined in these cases as in a homogeneous solution by the dissociation constants of the enzyme-substrate compound. On the other hand, the results obtained in the researches of Willstätter in the preparative purification of many enzymic substances, have demonstrated that, for the enzymes themselves, the active mass is determined solely by their concentration, and they are not at all, or not materially, influenced by alteration of the degree of dispersion and by surface variations.

"The view that a definite surface development is to be regarded as an essential preliminary for the activity of enzymes appears, it is true, to be supported by certain properties, especially in the more complicated reaction systems, as in that of the fat cleaving enzymes. Thus pancreatic lipase is found to be only partially active in some of its adsorbates, as in alumina and kaolin adsorbates, and hardly active at all in others, as the adsorbates of tristearin and cholesterin. However, these phenomena are not to be attributed to an injury of the adsorption ability but rather to an injury or repression of its specifically reactive grouping, for, in fact, the enzyme can be elutriated in a state of undiminished activity from the adsorbates mentioned," p. 48.

"The recognition of the synthesising action of enzymes lent interest also to the question as to whether they were able to effect displacements in the ordinary equilibria states of chemical reaction systems, i.e., whether enzyme equilibrium is to be regarded as identical with that effected by other catalysts. According to the laws of thermodynamics, it was to be expected that an enzymic catalyst, incapable of binding an essential portion of the reacting components, would cause no alteration of the usual equilibrium. The results obtained with enzymic equilibria have shown meanwhile that this requirement, apparently, is not fulfilled in all enzymic reactions, even though in many cases the point of the non-enzymic equilibrium cannot be definitely determined," p. 53.

"Armstrong has expressed the view that enzymes are capable of synthesizing only those substances which they do not hydrolyse, and that accordingly a distinction must be made between hydrolysing and synthesising enzymes. This is based on the results obtained by Emmerling according to which the disaccharide obtained by Croft Hill through the action of yeast extract on grape sugar is to be identified with isomaltose, hence with a substance which is not hydrolysed by the maltase of yeast, similar observations having also been made by Fischer and Armstrong. But this theory has not been supported by the extensive researches of Bourquelot and his school, not even with the carbohydrate-splitting enzymes, which they are held primarily to concern; thus it has been shown that, contrary to the particular theories of Armstrong, the glucosidase of bitter almonds is capable of forming the same glucosides which it hydrolyses. Furthermore, in the action of glucoside-splitting enzymes, according to Bourquelot, there is a formation of true equilibria, which can be reached from both sides, as well as the hydrolytic as by the synthetic procedure. Thus in an example of the hydrolysis or synthesis of β-methyl glucoside by emulsin in 30 percent methyl alcohol, the velocity of the two processes nearly coincided, hence there was obtained for the equilibrium constant $K = k_2/k_1$ the value 1, corresponding to a hydrolysis or synthesis of 50 percent," p. 56.

"According to Michaelis and Pechstein, the active complexes of amylase and anions are characterized by widely varying dissociation constants; the stability of the compound of enzyme and ion appears, for example, to decrease in the following sequence of ions: $NO_3{}'$ Cl', Br' $SO_4{}''$. This sequence is derived from the varying intensities of inhibition exerted by the ions on the enzyme, maximally activated by Cl-ions, under the assumption that a distribution of the enzymes takes place between the various ions and that the "chloride amylase" represents the most active, but not the most strongly united ion compound of the enzyme. The fact that various acidity optima correspond to the individual amylase complexes is explained by the assumption that they represent different types of amylases. The differences observed, however, are considered by Hahn and Harpuder as well as by Willstätter, Waldschmidt-Leitz, and Hesse as being due to the combined salt-buffer activation; the influence of the activators is of varying magnitude with different hydrogen numbers," p. 61.

"From the type of amylase activation which appears to be effected by various kinds of ions, and therefore to be non-specific, though it affects the entire operation of the enzyme and is therefore to be regarded as absolute, we must differentiate a *second type of enzyme activation*, which is characterized by the fact that it is capable of expressing itself only with respect to definite, particular affinities of an enzyme, or else with respect to *a definite stage of the reaction which it accelerates*; it is to be understood merely as relative and it is found to be much more specific, i.e., it is conditioned by the presence of specific activators. One of the best-studied examples of this is the activation of trypsin, the most important proteolytic enzyme of the pancreatic gland, by the enterokinase of the intestinal mucous membrane; this was discovered by Schepowalnikow, working in the Pawlow laboratory. It was demonstrated by this investigation that pure pancreatic fistula secretion was entirely inactive with respect to the hydrolysis, for example, of true proteins, and that it was not until it reached the intestine, by the addition of one of the mucous membrane juices, namely, enterokinase, it became active; this phenomenon was looked upon as an enzymic process, i.e., as a transformation of the trypsin from its zymogen into the active form. However, it has become possible only at a very recent date to recognize with certainty the true nature of this activation process. That is, it has recently been shown in an investigation by Waldschmidt-Leitz that the reaction between trypsin and enterokinase is based upon stoichiometric principles; and enzymic transformation of the "trypsinogen," as is termed, does not occur. There is formed rather a compound of the enzyme and the activator, in considerable measure dissociated, whose formation requires a certain length of time. It was found possible, after successful activation, to separate the enzyme and activator by adsorptive methods.

"Enterokinase, whose properties appear to resemble those of enzymic substances is to be regarded as a specific activator of trypsin; the reports in the literature with respect to activations of this enzyme by other substances, such as lime or gall salts, have proved to be incorrect. But the influence of enterokinase concerns only certain cases of enzyme action, i.e., the activator possesses merely the significance of a substance which assists in the cleavage of certain special structural combinations, such as are present for example in genuine proteins. As Wäldschmidt-Leitz and Harteneck have shown, trypsin is capable, even without activation by enterokinase, of hydrolyzing a series of substrates, such as protamine or peptone, with considerable rapidity, even though its action in these cases is strengthened by the addition of an activator because of the dissimilarity of the structural groupings present in the substrates. This activation of trypsin by enterokinase, which is relative and specific, must be distinguished, therefore, from those described for animal amylase, even if future researches should prove that in the enzymic hydrolysis of starch also the influence of the activators is operative only with respect to certain stages of the reaction," p. 62.

"The improvement in the preparative procedures for the production of the adsorbents and the extension of their analytical investigation make it possible, in newer works, to characterize some of the preparates as definite chemical individuals, as definite hydrates of aluminum oxide, and also to determine how they may be specifically obtained by methods capable of reproduction. Thus it has been found that the alumina preparate *C* obtained by cautious precipitation with dilute ammonia, corresponds to the composition of an ortho-aluminum hydroxide, having the formula $Al(OH)_3$. This alumina gel ($C\alpha$) which is obtained under the mildest conditions, is characterized, however, by the ease with which it suffers alteration; in aqueous suspension it is changed after a short time into a second compound ($C\beta$), which while likewise unstable, is more stable than the α modification and is then gradually transformed into the third modification ($C\lambda$). With these transformations, which are to be attributed to a chemical alteration of the molecule, whether it is an isomeric or a polymorphic phenomenon, there is connected an alteration of the basic and acid properties and of the adsorption behavior of the gels; they are not to be explained by alterations in the colloid state. Thus the alumina varieties A and B reveal themselves as polyaluminum hydroxides. *It was further found possible to obtain from the ortho-hydroxide of* aluminum, as likewise by the conditions of direct precipitation with long continued action of ammonia and a higher experimental temperature, a further definite hydrate, whose composition corresponds to the formula of a meta-hydroxide, AlO.OH; this hydrate, which has proved to be specially effective for the separation of the saccharase and maltase in yeast autolysates, possesses neither acid nor basic properties," p. 97.

"More recent investigations by Felix and Harteneck, with histone and by Weber and Gesenius with casein confirm the equivalence of NH_2 and COOH. Waldschmidt-Leitz and Künstner further demonstrate this constant relation of NH_2 and COOH formation with four typical proteins (egg albumin, casein, gelatin, and histone) and point out the cause of the divergent observations which have been reported. These divergencies in the direction of a stronger carboxyl increase are shown to be due to an incomplete determination of the intrinsic acidity of the unaltered substrate in the initial alkalimetric titration. This same *cause might be responsible for the* variations noted by Waldschmidt-Leitz and Simons in the hydrolysis of certain cereal proteins. Their unfavorable solubility behavior, however, does not permit a positive removal of the analytical sources of error," p. 133.

"Experiments show that this indifference of the trypsin toward adsorption by alumina in acid solution holds only for the stabile gel $Al(OH)_3$, designated as $C\lambda$, whereas, the trypsin is completely adsorbed by using an insufficiently aged alumina preparate, which contains varying quantities of the unstable β modification. The presence of this modification must be strictly excluded in order to carry out successfully the above separation procedure," p. 145

It has been shown that the action of hydrocyanic acid on papain is very similar to the reaction between trypsin and enterokinase. The combining of the activator with the enzyme is a reaction conditioned by time; in the case of papain a period of one hour is required for the action of hydrocyanic acid to attain maximum activation. Furthermore, the papain-HCN compound is marked by a considerable capacity for dissociation; the activator can be withdrawn from the activated enzyme by a diminution of pressure. *The activated and* the non-activated enzyme, papain-HCN and papain, whose optimal actions on gelatin correspond to a pH of 5.0, and whose activity-pH curves coincide, differ in their specificity; they behave as two specific proteolytic enzymes. The activation of trypsin by enterokinase results in an increase of the substrates susceptible to the enzyme, the increase being particularly in the direction of the genuine proteins. In the case of the plant enzyme, its action is extended by the action of the co-enzyme, hydrocyanic acid, but conversely to tripsin. the extension is in the direction of the lower protein degradation products, the peptones and also the polypeptides. Thus peptones, whether obtained by peptic or by papain digestion, are not attacked by papain alone, but are split in a progressive and extensive reaction by the combination of papain and hydrocyanic acid," p. 149.

"Using integrally pure enzymes preparates, Grassmann and Dyckerhoff have quantitatively separated and identified the fission products. *In all cases the end amino acid carrying the free amino group is the one split off from the polypeptide chain.* In the case of leucyl glycyl glycine, leucine and glycyl glycine were separated in almost quantitative yield. (The leucine is separated from the fission products by means of its difficulty soluble copper salt and the glycyl glycine as the ester chlorohydrate.) In the case of glycyl glycyl-l-leucine, the peptide is shown to be split into glycocoll and glycyl leucine. The peptide linkages in the remaining di- or tripeptide appear to be wholly resistant against further action of the enyzme in the reaction mixture. It is not entirely clear as to why the reaction comes to a complete standstill after liberation of one carboxyl group.

This strictly specific action of the enzyme stands in contrast to the unspecific course of alkali hydrolysis. Thus, Abderhalden and Brockmann recently showed that in the incomplete alkali hydrolysis of l-leucyl-glycyl-d-alanine, both leucyl glycine and glycyl alanine can be demonstrated.

"The fact that a free amino group in neighboring proximity to the peptide linkage is necessary for the action of the enzyme, is supported by the previous findings as to the resistance of peptide derivatives with substituted amino groups. Thus it has been shown that yeast polypeptidase splits neither benzol diglycyl glycine nor β-naphthalinsulfo-glycyl-tyrosine. These, however, are substrates for the action of pancreas trypsin, as has been shown by Waldschmidt-Leitz and co-workers," p. 162.

"The solubility behavior of the animal enzyme is very remarkable, varying considerably with the type of animal under investigation. Thus, the enzyme from the dog kidney is found to be completely soluble in aqueous media or glycerine, that of the swine kidney only partially soluble, and that of the horse kidney almost entirely insoluble. This phenomenon is to be explained not by the assumption of absolutely different enzymic individuals, but by a differing tenacity in the linkage between the enzyme and the insoluble associated materials," p. 169.

"Further new analytical discoveries concern the problem of the iron content of the peroxidase. In the researches of Gola as well as those of Willstätter and Stoll, the assumption was advanced and experimentally supported that the iron, which accompanies the peroxidase in all purification processes, is an integral constituent of the enzyme molecule. Analysis of the purer peroxidase preparates, however, has not confirmed the relation which appeared to exist between the iron content and the enzymic action. It is true indeed that iron compounds are obstinately associated with the enzyme, and accumulate at times in the course of the purification more plentifully than the peroxidase. But in the adsorption on kaolin from dilute solution and particularly in the precipitation of the peroxidase with tannin, a means has been found for deciding the question of the iron content. Elimination of the iron-containing foreign substance by tannin has been carried so far that a preparate concentrated 5-fold exhibited even a 7-fold less iron content, namely, 0.06 per cent. Hence the iron *is without significance for the constitution and color of the peroxidase*," p. 224

As was stated in the preface, the book is written from Willstätter's point of view. There is consequently nothing to show that Willstätter's assumptions in regard to the various aluminas, p. 97, are probably wrong. There is nothing to show that Sherman has been unable to confirm some of Willstätter's separations. Sumner's preparation of crystallized urease is rejected, p. 117, because Euler and Brunius were not able to duplicate Sumner's results when starting with a different raw material.

Wilder D. Bancroft

English and Science. *By Philip B. McDonald. 21 × 16 cm; pp. vii + 192. New York: D. Van Nostrand Company, 1929. Price: $2.00.* In the preface the author says: "In this modern age of science and industry we are compelled to think clearly and to speak and write concisely. A student of science, in particular, should express himself in as clear and concise a style as is possible. Yet much of the old-fashioned rhetoric and composition taught in our schools and colleges encourages verbosity and tolerates vague, stilted language. Such teaching is not suitable for the education of engineers, scientists, and most business and professional people. Nor should courses in composition for such students emphasize the writing of short stories, light essays, verse, or plays. The most important officials in modern civilization usually write only two kinds of compositions—letters and reports. In academic life, for example, deans write reports to the president of the university, and research-workers write reports of their discoveries; our daily newspapers frequently print extracts from significant reports of investigators, administrators, and experts. In the following pages the principles of simplicity and conciseness have been given first consideration. As much as possible of the hackneyed and obvious has been omitted, although the principle of repetition for emphasis has been used. A determined effort has been made to present an analysis of English for the professional man in a more interesting and readable form than books on this subject usually attain. Perhaps the professional man whose English is most in need of correction is the engineer. For that reason a number of suggestions in the book are addressed directly to him, but this does not mean that the suggestions are not applicable to other professions and businesses. *Technical specialists in general* are inclined to make the same mistakes in English. The engineer stands out because he represents a well-known type whose tastes are not exactly literary and whose good-nature does not resent constructive criticism. It is hoped that this book will be useful both to students of science in colleges and to those mature individuals who wish to improve their English. The last three chapters offer suggestions for cultural reading for the man of science and encourage the broadening of the specialized mind."

The chapters are entitled: the importance of written records; writing and presenting a technical paper; reports in formal, third-person style; reports in informal, first-person style; good letters and bad; correct language, the basis of all writing; obscurity, pomposity, and ornateness; the amateur's delights; conciseness, the cardinal secret of style; sentence structure; the difficult art of punctuation; mastering words; listed expressions; cultural reading for the technical student; an example of reading in the history of science; suggested readings about invention.

There is a great need for a book like this and this one seems to be written quite intelligently. The pages on how to present a technical paper are excellent. Most of us wish to tell the audience what we think they ought to hear, which is noble and praiseworthy but not effective. The reviewer would have liked to have seen stress laid on the importance of speaking very slowly, when talking to a large audience. A man with a poor voice can make himself understood if he will speak slowly enough.

On p. 101 the author says, quite correctly: "As a general rule, when a person uses a word or phrase a great deal, he probably is using it incorrectly part of the time, and he should curb his fondness for it and think up a synonym or two." A case in point is the author's use of the word, amateur.

On p. 118 the author approves the form: "If the other tests fail, he will determine by chemical tests the amount of sulphur in the powder." The reviewer prefers the form. "If the other tests fail, he will determine the amount of sulphur in the powder by chemical tests." Which is right, the professor of English or the professor of chemistry?

While there are occasional passages, about which there will be differences of opinion, the book is an admirable one and should be read by all chemists young and old. If the book will help an engineer—and the author says that it does—the chemist should get much more out of it.

Wilder D. Bancroft

1852

THE SYSTEM POTASSIUM METASILICATE-SILICA

BY F. C. KRACEK, N. L. BOWEN, AND G. W. MOREY

Introduction

The binary system K_2SiO_3-SiO_2 was studied as a preliminary to the ternary systems K_2O-CaO-SiO_2 and K_2SiO_3-Na_2SiO_3-SiO_2, both of which are now completed. While this binary system had never been investigated it was thought that the essential features could be deduced from the study of the ternary system H_2O-K_2SiO_3-SiO_2 by Morey and Fenner.[1] They determined the isothermal polybaric saturation curves from 285° to 600°C, and also the isobaric polythermal saturation curve at one atmosphere pressure of water vapor for mixtures containing SiO_2 to K_2O in the ratios of approximately 1:1 to 4:1, that is, from the metasilicate composition to beyond the tetrasilicate. The latter curve was believed not to be essentially different from the melting point curve of the binary system K_2SiO_3-SiO_2, the expected difference being that of the melting point lowering caused by the solution of H_2O in the molten liquid. This melting point lowering was determined for the $K_2O.SiO_2$ and $K_2O.2SiO_2$ compositions, whose melting points were found to be 976° and 1041°,[2] while in presence of one atmosphere of H_2O vapor the values were 942° and 1034°C respectively. By extrapolation from the hydrous system the binary eutectic between $K_2O.2SiO_2$ and quartz was placed at 525°C and 71.8 per cent SiO_2, that is, at a SiO_2/K_2O ratio of 4.0:1.

The present study of the anhydrous system, however, brought to light important additional features, making separate publication of the system desirable.

Since the appearance of the work of Morey and Fenner[3] there has been little other study of this system. Pukall[4] prepared glasses of SiO_2/K_2O ratios of 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1 by heating mixtures of $KHCO_3$ and SiO_2 without any attempts at systematic crystallization, and considered that the mixtures so prepared, whether crystalline or glassy, were compounds of the corresponding formulae, an altogether incompetent conclusion. Rice[5] studied the "deformation" eutectic temperatures of cones of K_2O-SiO_2 mixtures prepared by melting K_2CO_3 and SiO_2 to glasses, which were then powdered and sintered to make the cones. He gives 780° for the eutectic at 45 per cent SiO_2, 55 per cent K_2O, with a 10 per cent tolerance in composition, and 880° for a eutectic at 82.5 per cent SiO_2, with a 5 per cent tolerance. The former temperature checks closely with our results.

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[1] Morey and Fenner: J. Am. Chem. Soc., 39, 1173 (1917).

[2] Compare p. 1871

[3] Morey and Fenner: op. cit.; Morey: J. Am. Chem. Soc., 36, 215 (1914); Z. anorg. allgem. Chem., 86, 305 (1914).

[4] Pukall: Silikat Z., 2, 65 (1914).

[5] Rice: J. Am. Ceram. Soc., 6, 525 (1923).

Experimental

1. *Preparation of Materials.* The mixtures studied were prepared in the form of glasses by decomposing K_2CO_3 with quartz in platinum crucibles. The quartz was partly that used in previous silicate syntheses[1] and gave a residue of 0.07 per cent on evaporation with HF and H_2SO_4; partly another lot which gave a 0.05 per cent residue. The K_2CO_3 was a specially purified material, some of which was derived from especially pure $KHCO_3$. In preparing the glasses it is advisable to allow the well mixed ingredients to sinter at 700 to 800°C for several hours, in order to enable the reaction to proceed as far as possible without formation of appreciable amounts of liquid until most of the CO_2 is driven off. The temperature then can be gradually raised until the mixtures become fluid enough to enable bubbles of the remaining CO_2 to escape, without excessive frothing. For accurate synthesis of glasses of desired composition it is essential to guard against two main sources of loss, namely, mechanical loss caused by the bursting of bubbles of the escaping CO_2, and secondly, loss by volatilization of K_2O from the reacting mixture. The first loss can be kept to a minimum by accurate temperature control of the melting charge. The second loss is more difficult to control, but it also can be minimized if the melting after the preliminary sintering is done in electric furnaces where there are no violent gas currents to carry off the K_2O fumes, in preference to using gas furnaces. Without the preliminary sintering the violent escape of CO_2 from the exceedingly viscous glasses formed causes such excessive frothing as to make the preparation of glasses of desired composition uncertain.

After the first melting the glasses were crushed in a diamond mortar to pass a 48-mesh sieve and examined under the microscope for inequalities in composition. When necessary, they were then remelted, and the operation repeated until homogeneous mixtures were obtained.

The glasses were usually prepared of known composition by accurately weighing the amounts of ingredients used, followed by carefully checking the weight after each remelting. The slight loss by volatilization, assumed to be due to K_2O alone, was corrected for by the addition of known amounts of K_2CO_3. Numerous analyses were made, usually by the method described by Morey and Fenner,[2] in which the powdered glass was treated twice with HF, the residue dried at 125° and weighed as K_2SiF_6. This method is exceptionally convenient and accurate in this case. As a special precaution most of the analyses were checked by conversion to K_2SO_4 in the usual manner.

2. *Melting Point Determination Methods.* Most of the thermal study was carried out by the quenching method[3] using materials which had previously been crystallized by appropriate heat treatment, when necessary. In this method small quantities of the powdered material, amounting to a few

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[1] Morey and Bowen: J. Phys. Chem., 28, 1167 (1924); J. Soc. Glass Techn., 9, 226 (1925).

[2] Morey and Fenner: op. cit.

[3] Shepherd and Rankin: Am. J. Sci., 28, 293 (1909).

milligrams, are wrapped in thin Pt foil and held suspended in a furnace in close proximity to a thermocouple, at a desired constant temperature long enough for equilibrium to be attained. The charge is then quickly chilled to freeze the equilibrium, and examined under the microscope. The operation is repeated until a temperature is fixed such that just above it the charge remains in glassy condition, and just below it crystals are present. The crystals can be identified by the ordinary petrographic methods.

In addition to the quenching experiments, heating curves were made on several preparations by the differential thermocouple method. These will be described in detail later (see p. 1874).

The temperatures were measured by means of Pt vs. 90 Pt, 10 Rh thermocouples, using a highly sensitive potentiometer system. The thermocouples were calibrated at the fixed points NaCl 800.4°,[1] gold 1062.6°, Li_2SiO_3[2] 1201°, diopside 1391°,[2] and anorthite 1550°[2] and used with the aid of the tables of Johnston and Adams[3] together with an appropriate deviation curve. The couples were checked frequently at the NaCl and Li_2SiO_3 points to ensure that they had not suffered by contamination. The furnaces used were wound with Pt wire on alundum tubes and were maintained at constant temperature by means of the thermoregulator developed by Roberts[4] which has proved invaluable in the work of this Laboratory. The quenching charge was placed close to the hot thermocouple junction at the point in the furnace where there is practically no temperature gradient.

3. *Crystallization of the Preparations.* The length of time required for the initial crystallization and for the attainment of equilibrium in the melt, and the speed with which it was necessary to chill the charge in order to freeze the equilibrium varied greatly with the composition. Mixtures whose composition lies between $K_2O.SiO_2$ and $K_2O.2SiO_2$, and those containing in excess of 90 per cent SiO_2 crystallize rapidly when the glass is held near the liquidus temperature; to freeze the equilibrium in such mixtures it was found necessary in many cases to quench the charges by dropping them into cold mercury. All other mixtures could be chilled quickly enough by simply lifting them rapidly out of the furnace.

Preparations whose compositions are near that of $K_2O.2SiO_2$ devitrify readily enough for crystals to grow while the powdered glass is being brought up to the liquidus temperature. With increasing percentage of SiO_2 the crystallization velocity falls off very rapidly. Mixtures near $K_2O.4SiO_2$ are exceedingly difficult to crystallize, and indeed, it was found that without seeding with the appropriate crystalline phase even several weeks' time near the equilibrium temperature was insufficient to bring about the growth of an appreciable quantity of crystals. The pure crystalline compound $K_2O.4SiO_2$

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[1] Roberts: Phys. Rev., (2) 23, 386 (1924).

[2] Day, Sosman and Allen: "High Temperature Gas Thermometry," Carnegie Institution of Washington Publ. 157 (1911).

[3] Johnston and Adams: Am. J. Sci., 33, 534 (1912).

[4] Roberts: J. Opt. Soc. America, etc., 11, 171 (1925).

melts readily, but to attain equilibrium between these crystals and a melt of a different composition several days may be required.

Hydrothermal crystallization was found useful in inducing the initial formation of crystals in mixtures near the $K_2O.4SiO_2$ composition. For this purpose several 0.5 to 1.0 gram charges wrapped in thin Pt foil were suspended in a gold crucible containing 0.2 to 0.5 gram H_2O, and sealed inside a steel bomb[1] of approximately 40 cc capacity. The bomb was heated to 500-600° (the best temperature being found to vary with the particular compositions employed) and held at approximately constant temperature for 1 to 3 days. At the end of this time the charges were found well crystallized, except occasionally when more water was used than necessary. The water in the bomb must be insufficient to produce the vapor pressure of the two-phase liquid-vapor equilibrium, otherwise the amount absorbed by the silicate will produce an unsaturated solution and crystals can not form.

The hydrothermal method was useful not only in the crystallization of the $K_2O.4SiO_2$, but also in inducing quartz to form in the appropriate mixtures. The formation of the various crystalline forms of silica in the melt can be sharply controlled by the amount of H_2O in the bomb. In dry crystallization, or with only about 0.1 gram H_2O in a 40 cc bomb at 500°, crystals of tridymite or cristobalite are invariably produced. When the amount of H_2O is increased to 0.4 to 0.5 gram, quartz crystallizes out as well-formed, sharp-edged crystals. This result appears to be in accord with the Ostwald rule of successive reactions.

A peculiar phenomenon observed with mixtures near $K_2O.4SiO_2$ has not been satisfactorily explained. It was first seen in a preparation, SiO_2 = 65.4 per cent, which had been crystallized in a bomb, later heated for 3 days at 760°, of which the notes state: "Looks peculiar, as if 2 kinds of glass, immiscible. Outer glass n = 1.487; inner much higher. Inner is not all glass, but contains spherulitic crystallization." This became a homogeneous glass after 5 hours at 860°. The same preparation, initially glass, heated 10 hours at 800°, showed approximately 5 per cent of this material; reheated 44 hours at 800°, it had diminished to 2 per cent; the reheating continued 44 hours at 700° showed less than 1 per cent, some of which strongly suggested octahedra; the reheating continued 4 days at 700°, showed some $K_2O.2SiO_2$ as well as the above unknown material; reheated 6 days at 650°, showed almost none of this material, and a small amount of $K_2O.4SiO_2$; reheated 6 days at 650°, was about one-half $K_2O.2SiO_2$, $K_2O.4SiO_2$ and glass. Another preparation, SiO_2 = 65.8 per cent, in which $K_2O.2SiO_2$ had been crystallized by heating dry in 3 days at 760°, on further heating at 823°, had $K_2O.2SiO_2$ still present, as well as the material under discussion, in polyhedral outlines, but usually rounded patches and streaks, isotropic, n = 1.55. The material appeared to be concentrated around $K_2O.2SiO_2$ crystals. The material became entirely glass at 885° in 6 hours. A third preparation, SiO_2 = 73.7 per cent, which had been crystallized in the bomb, contained abundant material n = 1.55,

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[1] Morey and Fenner: op. cit.

very faint birefringence, which persisted at 908°. On this same preparation has been determined the stable liquidus for quartz at 851°, and the metastable liquidus for tridymite, at 834°. In none of the above preparations could the phenomena be obtained again; all were subjected to several treatments, and acted normally. We have no explanation to offer, but do not believe that it can correspond to any stable transformations.

Experimental Results

The results of the quenching experiments are assembled in Tables I and II; Table I gives the compositions of the mixtures, the temperature of primary crystallization, and the composition of the primary phase. In Table II are given enough of the quenching results to substantiate Table I; to give details of all the quenching experiments would require more space than would be justifiable. Table III gives the invariant points in the system and the properties of the crystalline phases. These latter are: the compounds $K_2O.SiO_2$ and

TABLE I

Composition and Melting Point Data

Number	t°C	Weight % SiO_2	Mol % SiO_2	Reference No.
	A. Solid phase: Cristobalite (SiO_2)			
—	1713	100.	100.	—
1	1635	95.5	97.0	M2947C
6	815(m)*	75.2	82.6	M2946A
	1470±	Transition Tridymite ⇆ Cristobalite		
	B. Solid phase: Tridymite (SiO_2)			
2	1254	82.3	88.0	M2947A
3	1149	79.8	86.1	K282
4	1038	77.5	84.4	K281
5	935	75.8	83.1	K280
7	905	74.8	82.3	K279
9	834(m)	73.7	81.0	K277
	C. Invariant point $K_2O.4SiO_2$+ SiO_2			
3	764±1	79.8	86.1	K282
4	764±1	77.5	84.4	K281
5	764±1	75.8	83.1	K280
7	765	74.8	82.3	K279
8	764	73.7	81.0	M32491
9	765	73.7	81.0	K277

* (m) = metastable.

TABLE I (continued)

Composition and Melting Point Data

Number	t°C	Weight % SiO_2	Mol % SiO_2	Reference No.
	D. Solid phase: Quartz (SiO_2)			
—	870 ± 10	Transition Quartz ⇆ Tridymite —		
9	840	73.7	81.0	K277
	E. Solid phase: $KO_2.4SiO_2$ (71.84 wt. % SiO_2)			
10	765	71.86	80.03	K284
11	764	71.7	79.9	M3248A
12	762 ± 2	70.9	79.3	M3149A
13	760 ± 4	70.1	78.6	K137, M3111
14	753	69.0	77.8	K283
17	745(m)	67.9	76.9	M33081
	F. Solid phase: $K_2O.2SiO_2$ (56.05 wt. % SiO_2)			
14	749(m)	69.0	77.8	K283
15	794	68.5	77.4	K278
16	825	68.0	77.0	K276
18	854	67.5	76.5	K275
19	893	66.8	75.9	K274
20	910	66.3	75.5	K266
21	923	66.0	75.3	K273
22	933	65.6	74.9	K272
23	954	64.8	74.3	K265
24	974	63.6	73.3	K259
25	980	63.2	72.9	K264
26	988	61.7	71.6	K253
27	992	61.0	71.0	K263
32	1036	56.2	66.8	K251
	G. Solid phase: Solid solution of $K_2O.2SiO_2$ with excess SiO_2			
28	1005	59.4	69.7	K258
29	1009	58.9	69.2	M2945B
30	1029	58.0	68.4	K256
31	1031	56.8	67.4	M2945A, K237
32	1036	56.2	66.8	K251

TABLE I (continued)

Number	t°C	Weight % SiO_2	Mol % SiO_2	Reference No.
H. Solid phase: Solid solution of $K_2O.2SiO_2$ with excess K_2O				
33	1035	55.7	66.4	K255
34	1034	54.6	65.4	K450
35	1027	53.4	64.3	M2946B
36	1016	52.4	63.3	K254
37	1000	51.7	62.7	K268
38	984	51.0	62.0	K257
39	968	50.5	61.5	K267
40	940	49.6	60.7	K448
41	943	49.6	60.7	K269
42	910	49.1	60.2	K262
43	895	48.8	59.9	K252
44	882	48.6	59.7	K270
45	835	47.7	58.8	K261
46	819	47.6	58.7	K271
K. Solid phase: $K_2O.2SiO_2$ (56.05 wt. % SiO_2)				
47	805	47.05	58.20	K260
48	783	45.9	57.1	K434
L. Additional preparations				
49	765	71.7		M3248H
50	764	72.2		MB8 Feb.

TABLE II

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
1	M2947C	1595	G + 30 m	Cristobalite, glass
		1635	G + 15 m	Rare cristobalite, glass
		1635	*Liquidus*; cristobalite (SiO_2)	
2	M2947A	1253	G + 30 m	Tridymite, glass
		1255	G + 30 m	Glass
		1254	*Liquidus*; tridymite (SiO_2)	
3	K282	1105	D + 4 h	Tridymite, glass
		1137	D + 2 h	Tridymite, glass
		1147	D + 2 h	Tridymite, glass
		1150	D + 3 h	All glass
		1149	*Liquidus*; tridymite (SiO_2)	
		763	B + 2 h	$K_2O.4SiO_2$, tridymite
		766	B + 6 h	No $K_2O.4SiO_2$; tridymite, glass

*G = glass.
D = crystallized dry.
B = crystallized in bomb.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
4	K281	994	D + 3 h	Tridymite, glass
		1034	D + 12 h	Rare tridymite, glass
		1044	D + 2 h	All glass
		1038	*Liquidus*; tridymite (SiO_2)	
		764	B + 5 h	$K_2O.4SiO_2$, much tridymite
		765	B + 6 h	No $K_2O.4SiO_2$, much tridymite, glass
5	K280	910	G + 10 h	Tridymite, glass
		934	G + 5 h	Rare tridymite, glass
		943	G + 3 h	About all glass
		943	*Liquidus*; tridymite (SiO_2)	
		764	B + 2 h	$K_2O.4SiO_2$, quartz, glass
		765	B + 3 h	Quartz, glass
		764	B_2 + 2 h	$K_2O.4SiO_2$, tridymite, glass
		765	B_2 + 3 h	Tridymite, glass
6	M2946A	812	22 h	Tridymite or cristobalite present
		815	*Liquidus*; tridymite or cristobalite	
7	K279	901	D + 12 h	Rare tridymite, glass
		906	D + 10 h	All glass
		905	*Liquidus*; tridymite (SiO_2)	
		764	B + 4 h	$K_2O.4SiO_2$, tridymite, glass
		765	B + 5 h	Doubtful if any $K_2O.4SiO_2$; tridymite, glass
8	M32491	759	D + 44 h	$K_2O.4SiO_2$, quartz, glass
		764	D + 24 h	Quartz, glass
9	K277	824	D + 10 h	Tridymite, glass
		834	D + 2 h	Rare tridymite, glass
		836	D + 3 h	All glass
		835	*Metastable liquidus*; tridymite	
		826	B + 3 h	Quartz, glass
		839	B + 18 h	Rare quartz, glass
		845	B + 50 h	All glass
		840	*Liquidus*; quartz	
		758	B + 50 h	$K_2O.4SiO_2$, quartz
		765	B + 7 h	Very rare $K_2O.4SiO_2$; quartz, glass

*G = Glass.
D = Crystalized dry.
B = Crystalized in bomb.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
10	K284	755	B + 12 h	Almost all $K_2O.4SiO_2$; may be some quartz
		764	B + 3 h	Almost all $K_2O.4SiO_2$; very rare quartz
		765	B + 3 h	Rare $K_2O.4SiO_2$; very rare quartz, glass
		767	B + 12 h	Very rare quartz, nearly all glass
		780	B + 12 h	Practically no quartz, glass
		765	*Liquidus*; $K_2O.4SiO_2$†	
11	M3248A	754	D + 18 h	$K_2O.4SiO_2$, some glass
		760	D + 18 h	$K_2O.4SiO_2$, glass
		765	D + 18 h	Glass
12	M3149A	747	G + 7 da	$K_2O.4SiO_2$ present
		760	D + 7 da	$K_2O.4SiO_2$, glass
		764	D + 7 da	Glass
13	K137	750	G + 15 da	$K_2O.4SiO_2$ present
	M3111	764	D + 7 da	Glass
14	K283	730	G + 3 da	$K_2O.2SiO_2$, much glass
		748	D + 3 da	Rare $K_2O.2SiO_2$, glass
		750	D + 1 da	All glass
		720	D + 7 da	$K_3O.4SiO_2$ present
		753	3 da more	Very rare $K_2O.4SiO_2$, glass
		755	2 da more	Glass
		749	*Metastable liquidus*; $K_2O.2SiO_2$	
		753	*Liquidus*; $K_2O.4SiO_2$	
15	K278	773	D + 7 h	Much $K_2O.2SiO_2$, glass
		790	D + 5 h	$K_2O.2SiO_2$, glass
		794	D + 5 h	Very rare $K_2O.2SiO_2$, glass
		800	D + 11 h	Glass
		794	*Liquidus*; $K_2O.2SiO_2$	
16	K276	802	G + 12 h	$K_2O.2SiO_2$, glass
		819	D + 6 h	Moderate amount of $K_2O.2SiO_2$, glass
		824	D + 4 h	Rare $K_2O.2SiO_2$, glass
		826	D + 3 h	All glass
		825	*Liquidus*; $K_2O.2SiO_2$	

*G = Glass.
D = Crystalized dry.
B = Crystalized in bomb.

† This preparation has composition of $K_2O.4SiO_2$; the persistence of quartz above the temperature at which $K_2O.4SiO_2$ disappears is to be ascribed to slow dissolution of quartz in melt, most probably. The possibility of incongruent melting of $K_2O.4SiO_2$ is not excluded, however. See text, p. 1873.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
17	M3308	745	G + 7 da	Very rare $K_2O.4SiO_2$, glass
		764	G + 1 da	$K_2O.2SiO_2$, glass
		773	G + 1 da	$K_2O.2SiO_2$, glass
18	K275	843	D + 3 h	$K_2O.2SiO_2$, glass
		854	D + 3 h	Rare $K_2O.2SiO_2$, glass
		855	D + 6 h	All glass
		854	*Liquidus*; $K_2O.2SiO_2$	
19	K274	845	G + 4 h	Abundant $K_2O.2SiO_2$, glass
		890	D + 2 h	$K_2O.2SiO_2$, glass
		893	D + 12 h	Practically all glass
		893	*Liquidus*; $K_2O.2SiO_2$	
20	K266	850	G + 5 h	Abundant $K_2O.2SiO_2$, glass
		900	G + 13 h	$K_2O.2SiO_2$, glass
		910	D + 12 h	Very rare crystals, glass
		913	D + 12 h	All glass
		910	*Liquidus*; $K_2O.2SiO_2$	
21	K273	876	G + 6 h	$K_2O.2SiO_2$, glass
		898	G + 4 h	Crystals, glass
		920	G + 5 h	Very rare crystals, glass
		926	G + 12 h	Glass
		923	*Liquidus*; $K_2O.2SiO_2$	
22	K272	875	G + 6 h	$K_2O.2SiO_2$, glass
		932	G + 4 h	Rare crystals, glass
		938	G + 6 h	Glass
		935	*Liquidus*; $K_2O.2SiO_2$	
23	K265	933	G + 5 h	$K_2O.2SiO_2$, glass
		943	G + 12 h	Crystals, glass
		950	G + 1 h	Sparse crystals, glass
		955	G + 1 h	Glass
		954	*Liquidus*; $K_2O.2SiO_2$	
24	K259	961	G + 2 h	$K_2O.2SiO_2$, glass
		974	G + 2 h	Rare crystals, glass
		975	G + 3 h	Glass
		974	*Liquidus*; $K_2O.2SiO_2$	

*G = Glass.
D = Crystalized dry.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating[*]	Condition after heating
25	K264	973	G + 4 h	$K_2O.2SiO_2$, glass
		978	G + 2 h	Rarish crystals, glass
		980	G + 5 h	Very rare crystals, glass
		983	G + 12 h	All glass
		980	*Liquidus*; $K_2O.2SiO_2$	
26	K253	974	G + 2 h	Crystals, glass
		985	G + 3 h	Rare crystals, glass
		988	G + 1 h	Rare crystals, glass
		988	G + 12 h	All glass
		988	*Liquidus*; $K_2O.2SiO_2$	
27	K263	984	G + 2 h	Abundant crystals (*ca* 50%) glass
		991	G + 3 h	Moderate amount of crystals
		993	G + 3 h	Glass
		992	*Liquidus*; $K_2O.2SiO_2$	
28	K258	988	G + 2 h	At least 50% crystallized, glass
		1003	G + 3 h	Abundant crystals, glass
		1006	G + 12 h	All glass
		1005	*Liquidus*;	$K_2O.2SiO_2$ solid solution, excess SiO_2
29	M2945B	993	Abundant crystals, glass	
		1008		Crystals, glass
		1009		Glass
		1009	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess SiO_2	
30	K256	1016	G + 2 h	More than 50% crystals, glass
		1028	G + 2 h	Abundant crystals, glass
		1030	G + 2 h	All glass
		1029	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess SiO_2	
31	M2945A	1000	G + 2 h	Largely crystallized, little glass
	K237	1029	G + 2 h	Abundant crystals, glass
		1032	G + 3 h	All glass
		1031	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess SiO_2	
32	K251	1032	G + 2 h	Crystals $K_2O.2SiO_2$, very little glass
		1034	G + 2 h	Crystals, very little glass
		1036	G + 2 h	Small trace of crystals, glass
		1036	*Liquidus*; $K_2O.2SiO_2$	

[*] G = Glass.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
33	K255	1031	G + 1.5 h	More than 50% crystals, glass
		1036	G + 2 h	Very rare, if any, crystals
		1035	*Liquidus*; $K_2O.2SiO_2$	
34	K450	1031	G + 5 h	About half crystals, glass
		1034	G + 3 h	Abundant crystals, glass
		1035	G + 3 h	Glass
		1034	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
35	M2946B	993	1 h	Nearly all crystals $K_2O.2SiO_2$
		1025	17 h	Crystals, glass
		1026	1 h	Rare crystals
		1028	1 h	Glass
		1027	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
36	K254	1015	G + 3 h	Moderately rare crystals, glass
		1018	G + 12 h	All glass
		1016	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
37	K268	995	G + 10 h	Moderately abundant crystals, glass
		1000	G + 2 h	Very rare crystals, glass
		1000	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
38	K257	983	G + 12 h	Crystals, glass
		985	G + 2 h	All glass
		984	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
39	K267	958	G + 3 h	Moderately rare crystals, glass
		967	G + 4 h	Moderately rare crystals, glass
		970	G + 3 h	All glass
		968	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
40	K448	931	G + 2 h	Abundant crystals, glass
		937	G + 2 h	Crystals, glass
		942	G + 2 h	Glass
		940	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
41	K269	941	D + 5 h	Moderately abundant crystals, glass
		948	D + 2 h	All glass
		943	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	

*G = Glass.
D = Crystalized dry.

TABLE II (continued)

Quenching Data

No.	Reference	t°C	Material and time of heating*	Condition after heating
42	K262	899	D + 4 h	Crystals, glass
		906	D + 3 h	Rare crystals, glass
		910	D + 3 h	Rare, if any crystals, glass
		910	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
43	K252	880	G + 3 h	Crystals, glass
		893	G + 3 h	Rare crystals, glass
		894	G + 12 h	Rare crystals, glass
		900	G + 3 h	Glass
		895	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
44	K270	875	1 h	Crystals, glass
		881	1 h	Rare crystals
		883	1 h	Glass
		882	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
45	K261	824	G + 12 h	Abundant crystals
		834	D + 4 h	Crystals, glass
		837	G + 4 h	All glass
		835	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
46	K271	815	D + 2 h	Crystals, glass
		817	D + 2 h	Crystals, glass
		821	D + 2 h	Glass
		819	*Liquidus*; $K_2O.2SiO_2$ solid solution, excess K_2O	
47	K260	795	D + 3 h	$K_2O.2SiO_2$, glass
		805	D + 14 h	Sporadic crystals, glass
		805	D + 2 h	All glass
		805	*Liquidus*; primary phase $K_2O.2SiO_2$	
48	K434	773	D + 3 h	Abundant $K_2O.2SiO_2$, probably some $K_2O.SiO_2$, glass
		785	D + 2 h	Very rare $K_2O.2SiO_2$
		785	*Liquidus*; primary phase $K_2O.2SiO_2$	
49	M3248H	758	D + 2 da	Much $K_2O.4SiO_2$, some glass
		762	D + 3 da	About 10% $K_2O.4SiO_2$, glass
		765	D + 2 da	Trace of crystal, glass
		765	*Liquidus*; $K_2O.4SiO_2$	
50	MB8 Feb.	762	D + 3 da	Small amount of crystals, glass
		765	D + 2 da	All glass
		764	*Liquidus*; $K_2O.4SiO_2$.	

*G = Glass.
D = Crystalized dry.

TABLE IIIa

Invariant Points

Crystalline Phase (s)	Reaction	% SiO_2	t°C
Cristobalite	Melting	100.	1713
Cristobalite-tridymite	Inversion	89.2	1470
Tridymite-high quartz	Inversion	74.4	870
High quartz-$K_2O.4SiO_2$	Eutectic	72.0	764
$K_2O.4SiO_2$	Melting	71.84	765
$K_2O.4SiO_2$-$K_2O.2SiO_2$	Eutectic	69.0	752
$K_2O.2SiO_2$	Breaking up of mix crystals	59.8	993
$K_2O.2SiO_2$	Melting	56.95	1036
$K_2O.2SiO_2$	Breaking up of mix crystals	47.6	814
$K_2O.2SiO_2$-$K_2O.SiO_2$	Eutectic	45.5	775
$K_2O.SiO_2$	Melting	38.94	976

TABLE IIIb

Properties of the Crystalline Phases*

Compound	Crystal System	Habit	2V	Optic sign	Refractive Indices γ	β	α
SiO_2: quartz	Hexagonal	Bipyramids	0°	pos.	1.553	1.544	1.544
SiO_2: tridymite	Pseudo-hexagonal	Plates	—	—	1.473	—	1.469
SiO_2: cristobalite	Pseudo-cubic	Octahedra	—	—	1.487	—	1.484
$K_2O.4SiO_2$	—	Plates, twinning	Large	pos.	1.482	—	1.477
$K_2O.2SiO_2$	Ortho-rhombic	Plates, cleavage	Large	neg.	1.513	—	1.503
$K_2O.SiO_2$	Ortho-rhombic(?)	(Granular)	*Ca.*35°	pos.	1.528	—	1.520

$K_2O.2SiO_2$, previously described by Morey and Fenner, the compound $K_2O.4SiO_2$, which is new, and the forms of silica, high quartz, tridymite and cristobalite, which crystallize from the appropriate preparations.

The data of Tables I and II are represented graphically in Figs. 1 and 2; in the latter the new points are represented by the black circles. For the purpose of comparison some of the results of Morey and Fenner are included, their points being marked by the open circles.

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* Description of the various forms of SiO_2 is taken from Morey and Bowen: J. Soc. Glass Techn., 9, 263 (1925).

1. *The compound* $K_2O.SiO_2$.—The properties of this compound have been partly described by Morey and Fenner.[1] It forms probably orthorhombic crystals, biaxial, positive, 2V approximately 35°, strong dispersion $\nu > \rho$. Its refractive indices are $\gamma = 1.528$, $\alpha = 1.520$, birefringence moderate ($\gamma - \alpha = 0.008$).

It melts congruently at 976°, and the melt crystallizes readily.

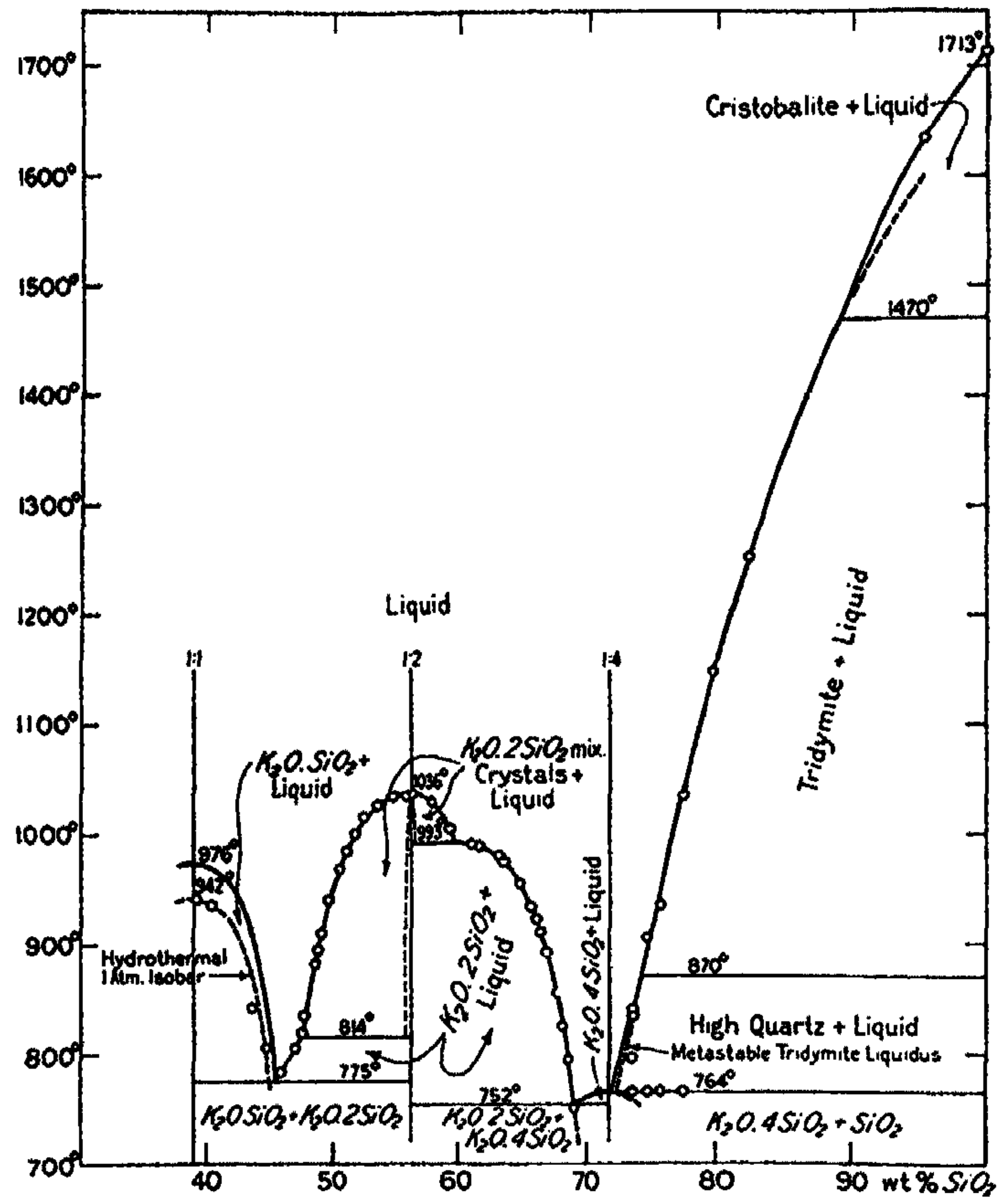

FIG. 1

Temperature-composition diagram of the binary system $K_2O.SiO_2$–SiO_2.

2. *The compound* $K_2O.2SiO_2$. The properties of the compound have been partly described by Morey and Fenner.[1] It forms orthorhombic crystals which are optically negative, with a large value of 2V, and a low birefringence. There is a micaceous cleavage parallel to $\gamma - \beta$. The refractive indices are: $\alpha = 1.503$, $\gamma = 1.513$.

Thruout the range of compositions over which $K_2O.2SiO_2$ is found to be present in contact with an equilibrium melt the crystals exhibit constant

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[1] Morey and Fenner: J. Am. Chem. Soc., 36, 215 (1914); 39, 1173 (1917).

optical properties regardless of the fact that the course of the liquidus curve (see sections 4 and 8) presents rather unusual features.

It has an enantiotropic inversion at 590°, and the high temperature form takes into solid solution small amounts of both K_2O and SiO_2. The melting point obtained in this work is 1036°, as compared with the value of 1041°, obtained by Morey and Fenner, and of 1015°, by Niggli.[1] The present value of 1036° is to be preferred to the previous one.

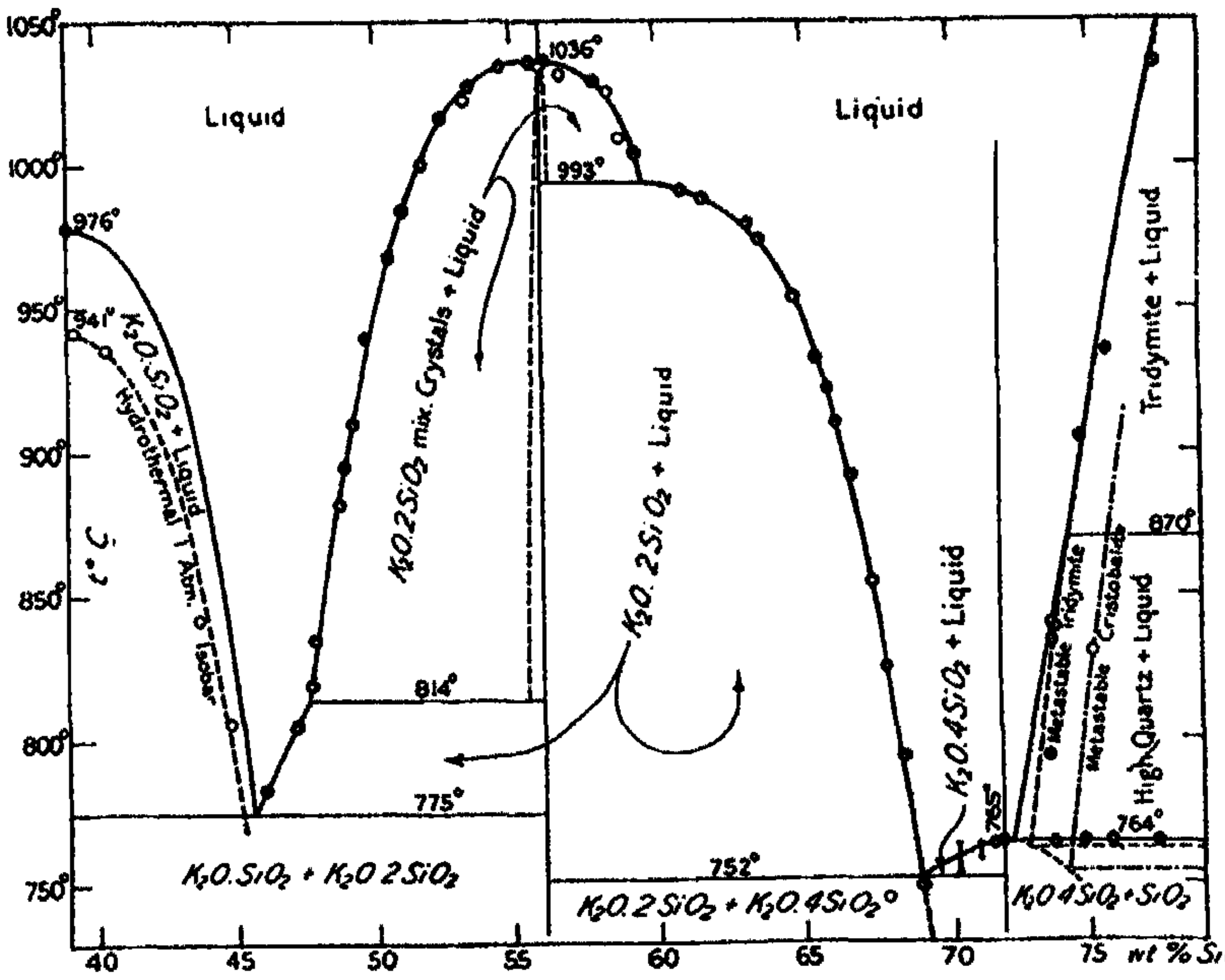

FIG. 2

Temperature-composition diagram of the binary system $K_2O.SiO_2$–SiO_2 to 1050° C. and 80 per cent SiO_2

3. *The compound $K_2O.4SiO_2$.* The best sample obtained of this newly discovered compound consisted of composite plates which looked uniform in broad section, but showed a complicated intergrowth or twinning in transverse section, and then showed inclined extinction. It is apparently biaxial, positive, with large 2V, but this is not very reliable. Its refractive indices are $\alpha = 1.477$, $\gamma = 1.482$. It melts, probably congruently, at 765°.

4. *The liquidus curve of $K_2O.2SiO_2$.* (See Fig. 2). The liquidus curve of potassium disilicate falls to the eutectic between $K_2O.SiO_2$ and $K_2O.2SiO_2$ at 775° and 45.5 weight per cent SiO_2 on the K_2O side of its congruent melting point, and to the eutectic between $K_2O.2SiO_2$ and $K_2O.4SiO_2$ at 752° and 69.0 weight per cent SiO_2 on the SiO_2 side. Each branch of this melting point curve shows a break, at 814° and 993° respectively. The fact that

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[1] Niggli: J. Am. Chem. Soc., 35, 1694 (1913).

these breaks do not occur at the same temperature on the two sides of the $K_2O.2SiO_2$ composition rules out the possibility of an inversion of the compound in this temperature region. The simplest explanation of the apparently anomalous course of this liquidus seems to be that crystals of $K_2O.2SiO_2$ dissolve an excess of either K_2O or SiO_2, depending upon the composition of the melt in equilibrium with the crystals, and that the resulting solid solutions then break up into the pure compound and a melt when the appropriate temperatures are reached. This question will be discussed further in connection with the description of the heating curves in a later section.

5. *The liquidus curve of* $K_2O.4SiO_2$. The melting curve of the tetrasilicate presents no unusual features. The curve rises from 752° and 69.0 weight per cent SiO_2, the eutectic between $K_2O.2SiO_2$ and $K_2O.4SiO_2$, to the melting point of the compound at 765°. The curve then meets the quartz liquidus very near the $K_2O.4SiO_2$ composition, the eutectic between the latter compound and high quartz lying at 764-5°. The results on preparation 10 (Table II) are of interest in this connection. The composition of this mixture is almost exactly $K_2Si_4O_9$ (71.84 weight per cent SiO_2 theor.). When crystallized in the bomb at 550°, using 0.4 gram H_2O, it was found to be 100 per cent crystalline, the properties of the crystals showing them to be almost wholly $K_2O.4SiO_2$, with only a faint trace of a more highly birefringent phase present. Heated in the quenching furnace at 765° for over 10 hours the $K_2O.4SiO_2$ crystals were found to have completely disappeared, but a small quantity of quartz remained in the quench. Heating for a much longer time at 765° did not appreciably modify the results. Traces of quartz were found even after heating 12 hours at 767°, while heating at 765° for only 30 minutes left traces of both $K_2O.4SiO_2$ and quartz. Because of the sluggish dissolution of quartz, too much significance must not be attributed to the presence of traces of it in the melt. The result is nevertheless interesting since it indicates a tendency of the compound $K_2O.4SiO_2$ toward incongruent melting.

In order to obtain further information on this point, to a mixture of preparation 50 (Table I), completely crystallized to $K_2O.4SiO_2$, was added enough finely ground quartz to give 72.3 per cent SiO_2, the mixture ground together in an agate mortar under alcohol, then ground dry. The resulting mixture was exceedingly finely ground, with only a few residual fragments of quartz as large as 0.001 mm in diameter. Heated for 7 days at 755°, all of the disilicate and almost all of the quartz had dissolved, the few quartz fragments remaining representing the larger grains. In view of the known slow rate of solution of quartz, it was believed that these too would have dissolved on longer heating, but this may not be the case. Heated 7 days at 751°, both quartz and disilicate remained. This would indicate that the $K_2O.4SiO_2$ has a congruent melting point, and that the maximum temperature of the $K_2O.4SiO_2$-quartz eutectic is 755°. The differences here are very small, and near the limits of precise determination of composition, at which there can be certainty of temperature control over the long periods of time necessary for equilibrium.

6. *The liquidus curve of Quartz.* High quartz crystallizes as a primary phase from mixtures between 72.0 and 72.4 weight per cent SiO_2, over the temperature range from 764.5° to 870°; at the latter point quartz ceases to be the stable phase and inverts slowly into tridymite. Quartz ordinarily does not crystallize readily from dry melts; to determine the liquidus temperature where it is the primary phase it has been necessary to resort to previously crystallized preparations in which quartz was produced by hydrothermal crystallization as described on p. 1860. Quartz, further, disappears very slowly from the heated samples, a point which has already been emphasized by Morey and Bowen[1] in their work on the system Na_2SiO_3-SiO_2. The quartz liquidus curve otherwise presents no special features.

7. *The Tridymite and Cristobalite liquidus.* Tridymite is the stable primary phase between 870° and 1470°, these temperatures representing the respective inversions of quartz to tridymite and tridymite to cristobalite according to Fenner.[2] Above 1470° cristobalite is the primary phase to 1713°, its melting point.[3,4] Several points were determined along these two branches of the liquidus, which present no special points of interest. Both tridymite and cristobalite are remarkable for the tendency to separate from the melts in metastable regions, and it has been possible to determine their metastable liquidus in several preparations, as will be seen by reference to Fig. 2 and to the tables of results.

In view of the difficulty of crystallizing $K_2O.4SiO_2$, we thought it might be possible to realize the metastable eutectic between $K_2O.2SiO_2$ and tridymite. For this purpose, well crystallized $K_2O.2SiO_2$ and a glass containing 74.92 per cent SiO_2, in which a fair amount of tridymite had been grown, were mixed in the proportions of $K_2O.4SiO_2$, finely ground together under alcohol, and heated at various temperatures. In 2 days at 646° all the crystals had dissolved, with the exception of very rare tridymite grains, which probably would have disappeared on further heating. After 4 days at 540° all the crystals had disappeared. After 8 days at 498° the disilicate had all dissolved, but there was still well-distributed tridymite, indicating that the metastable liquidus, with tridymite as primary phase, is ±520° for this mixture.

8. *Heating curve study of the $K_2O.2SiO_2$ liquidus.* It seemed desirable to further investigate the phenomena connected with the crystallization of $K_2O.2SiO_2$. The unusual course of the melting curve of this compound, derived from the quenching results, already described in section 4, leads to the supposition that $K_2O.2SiO_2$ is capable of forming mixed crystals with both excess of K_2O and of SiO_2, depending upon the composition of the melt

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[1] Morey and Bowen: J. Phys. Chem., **28**, 1167 (1924).

[2] Fenner: Am. J. Sci., **36**, 331 (1913).

[3] Greig: Am. J. Sci., **13**, 7 (1927).

[4] Ferguson and Merwin: Am. J. Sci., **46**, 417 (1918).

with which they are in equilibrium. It was thought that thermal analysis could throw some further light on this question.

It is well known that heating and cooling curves ordinarily yield little decisive information on the behavior of silicates, owing to the comparatively sluggish reactions and low changes in heat capacity accompanying the phase changes. This difficulty has been kept in mind in designing the apparatus, which was so arranged as to eliminate outside disturbances as much as possible, consistent with securing maximum sensitivity of reading. The apparatus has been described in another paper by one of us,[1] hence only the essential features will be mentioned here. A differential thermocouple arrangement was used employing Au-Pd vs. Pt-Rh (40% Pd, 10% Rh) couples, calibrated at the NaCl (800.4°) and Au (1062.6°) points. The e.m.f. of these couples changes approximately 50 microvolts per degree C, so that with a highly sensitive potentiometer system it is possible to read the differential temperatures to 0.01°. The furnace was designed to minimize convection currents. The charge and neutral body were placed in the furnace at the point of practically no thermal gradient. Slow, controlled rates of heating, of the order of 0.5° to 1.0° per minute were easily realized and storage battery current was used to eliminate further sources of error.

Owing to the great tendency toward supercooling, no usable results could be obtained with cooling curves. The arrests on the heating curves were not large, except for the heat effect accompanying the melting of the almost pure $K_2O.2SiO_2$ (preparation 32). Upward of 50 heating curves on the several preparations were established. The results are collected in Table IV. The typical course of the curves is depicted in Fig. 3 in which the curves are superimposed upon the same temperature scale, the ordinate representing the differential temperature between the charge and the neutral body. The principal feature of the curves is the location of the thermal arrests, which coincide closely with the temperatures at which breaks occur in the liquidus curve, as shown in Figs. 1 and 2.

An unexpected feature of the heating curves is the occurrence of an enantiotropic inversion in $K_2O.2SiO_2$ at 590°. The presence of this inversion has not been suspected before. It occurs at the same temperature in all the preparations studied, hence the crystals undergoing inversion, both the high and the low temperature forms, must be essentially the pure compound in the neighborhood of the inversion temperature.

In addition to the eutectic arrests at 775° and 750°, the curves show heat effects at about 810° and 980-990° on the two sides of the $K_2O.2SiO_2$ composition, respectively, corresponding to the breaks in the liquidus curves. The nearly pure $K_2O.2SiO_2$ (preparation 32) shows these breaks to an almost imperceptible extent. This conclusively rules out the possibility of an inversion at these temperatures, particularly since in the other preparations studied the arrests become more noticeable as the composition departs further from that of the compound. The simplest assumption that will explain

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[1] Kracek: J. Phys. Chem., 33, 1281 (1929).

TABLE IV

Results of Heating Curves

Number*	Phase reaction	Temperature °C
40	Inversion begins	590
	Inversion ends	597
	First arrest	775, 773
	Second arrest	811, 804
	Melting ends	940, 940
	M.p. by quenching	940
36	Inversion begins	588
	Inversion ends	596
	First arrest	799, 781, 775
	Second arrest	810, 801, 810
	Melting ends	1012, 1012
	M.p. by quenching	1016
34	Inversion begins	588
	Inversion ends	595
	First arrest	770
	Second arrest	810
	Melting ends	1035
	M.p. by quenching	1034
32	Inversion begins	591, 586, 585, 584, 588, 587, 587
	Inversion ends	596, 596, 596, 596, 597, 595, 596
	First arrest (feeble)	771, 776
	Second arrest (feeble)	805, 807, 817
	Third arrest (feeble)	980
	Melting ends	1036, 1035, 1038
	M.p. by quenching	1036
30	Inversion begins	592
	Inversion ends	596
	First arrest	760, 750
	Second arrest	981, 985, 978, 984, 990, 995
	Melting begins	1012, 1005, 1006, 1016
	Melting ends	1046, 1035, 1035, 1030
	M.p. by quenching	1029
28	Inversion begins	588
	Inversion ends	594
	First arrest	750
	Second arrest	983, 993
	Melting ends	1009
	M.p. by quenching	1005

* Refer to Table I for composition.

these arrests is, as has already been stated (p. 1873), the crystallization of solid solutions from the melt, which then decompose into the pure high temperature form of $K_2O.2SiO_2$ and liquid at 814° and 993°, on the two sides of the composition of the compound. As far as we know, there is no similar case of this type in the literature.

The melting points found by the heating curves do not differ essentially from those found by the quenching method (compare Tables II and IV), showing that the crystallized preparations melt readily enough for equilibrium to be attained during the time the preparation passes thru the melting arrest. Crystallization of $K_2O.2SiO_2$ from the molten preparation, on the other hand, is accompanied by enormous undercooling, as the following experiment will show. Molten $K_2O.2SiO_2$ (preparation 32) was allowed to cool with the furnace, no current passing thru the winding, from about 1100°C. No arrest was noticed during the cooling. The cooling of the furnace was then stopped at about 400°. Next day the temperature was gradually raised preliminary to a run, which was made as soon as the differential temperature came to a steady value. The course of this run is shown in Fig. 4. The inversion arrest at 590° was absent. On further heating a heat evolution began at about 670°, reached a maximum effect at 720°, and continued until

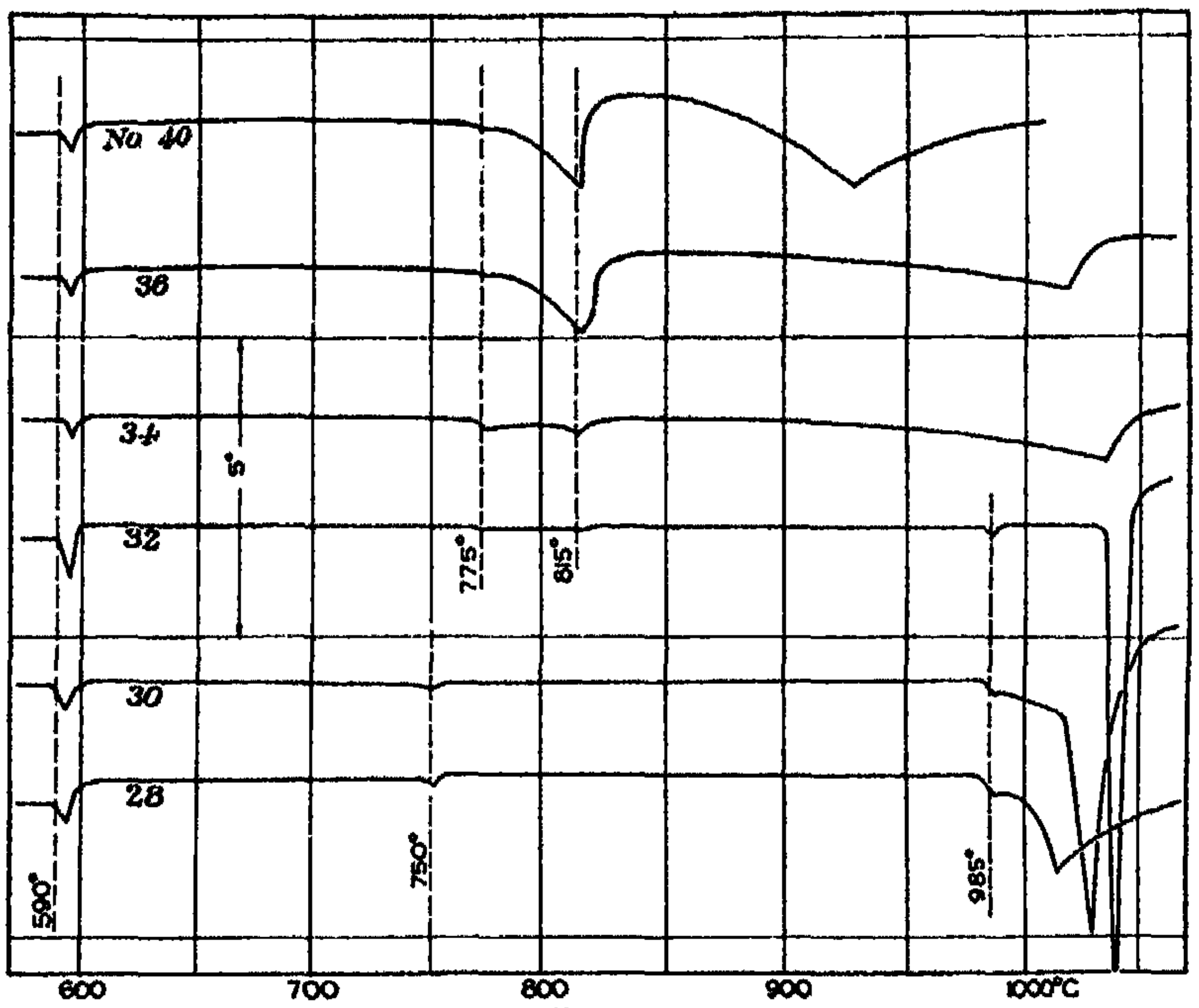

Fig. 3

Differential heating curves on preparations in the $K_2O.2SiO_2$ field. The ordinates are the differential temperatures between the sample and a neutral body. The numbers 28 to 40 refer to compositions in Tables I and IV.

approximately 800°. At this temperature the differential temperature again became steady; the melting arrest then followed in the normal manner. It is not surprising, then, that the tetrasilicate mixtures crystallize with difficulty if we bear in mind that the tetrasilicate liquidus lies at a temperature at which the crystallization of the much more easily devitrified disilicate proceeds with only moderate speed.

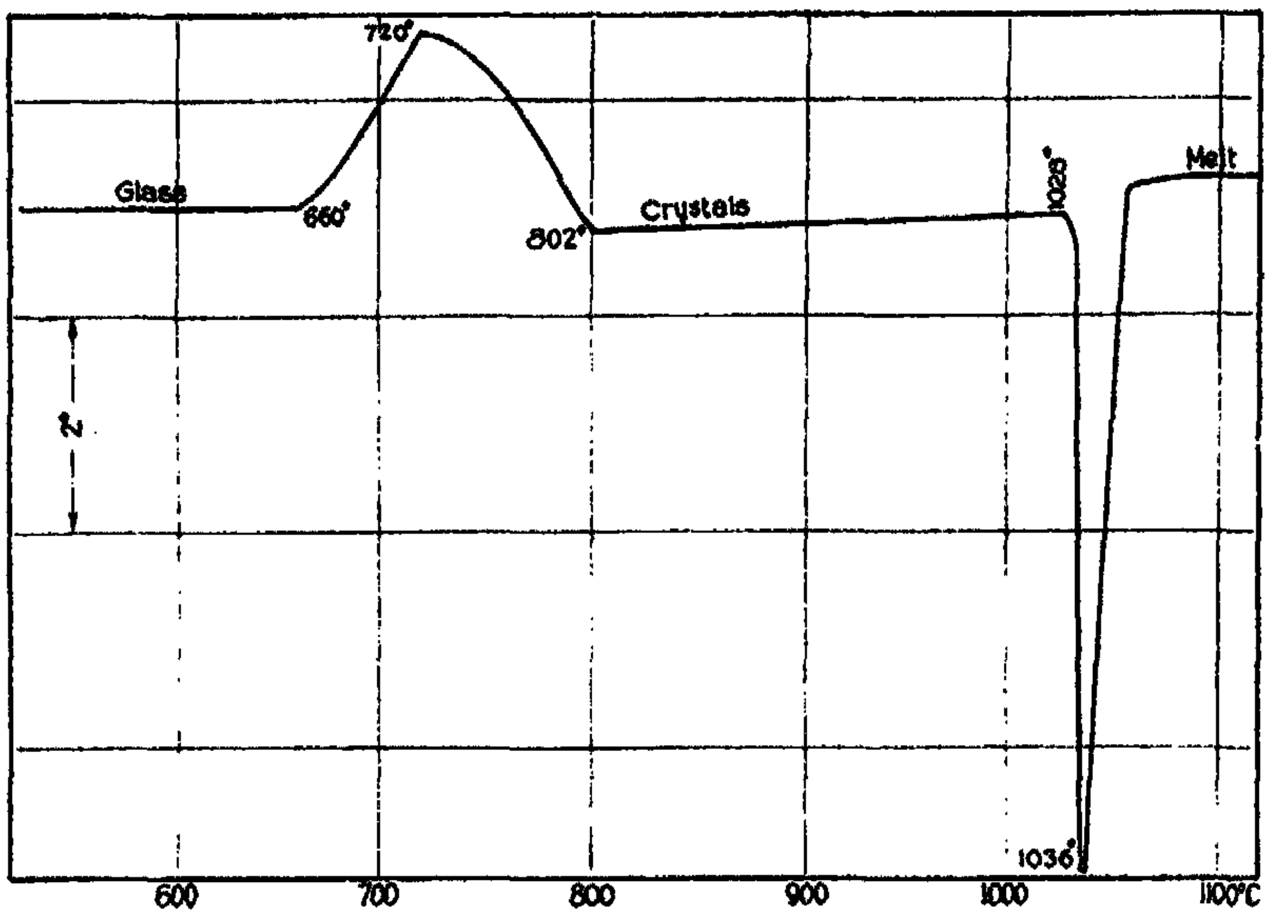

Fig. 4

Differential heating curve showing the crystallization of glass of preparation 32, nearly pure $K_2O.2SiO_2$.

Discussion and Conclusion

The system K_2SiO_3-SiO_2 finds application in the study of many petrologically important polycomponent systems, and in addition it is of technical importance in glass technology. The somewhat detailed study of the system presented here is therefore a logical preliminary step toward the three-component systems to which it contributes, besides possessing considerable independent significance.

The new results are in substantial agreement with the earlier work of Morey and Fenner on the hydrothermal system. The principal points of departure are the unusual contour of the disilicate liquidus and the presence of the hitherto unsuspected compound, $K_2O.4SiO_2$.

From the standpoint of inorganic chemistry the system is important in showing the trend within a group of the periodic system. Lithium enters into the formation of orthosilicate, metasilicate and disilicate, only the metasilicate $Li_2O.SiO_2$, apparently, having a congruent melting point. Sodium forms the congruently melting $Na_2O.SiO_2$ and $Na_2O.2SiO_2$; nothing is known about the orthosilicate, Na_4SiO_4. Potassium exhibits, in addition to the congruently melting $K_2O.SiO_2$ and $K_2O.2SiO_2$ another compound, $K_2O.4SiO_2$. Many references have been made in the literature to compounds of the general formula $2Me_2O.5SiO_2$ supposed to be formed by the alkalis. It is significant that in no case investigated with competent methods have such compounds been found at the liquidus.

Summary

The system K_2SiO_3-SiO_2 contains three compounds, $K_2O.SiO_2$, $K_2O.2SiO_2$ and $K_2O.4SiO_2$ whose melting points are 976°, 1036° and 765° respectively. The respective eutectics between these compounds are at 775° and 45.5 weight per cent SiO_2, and 752° and 69.0 weight per cent SiO_2. The eutectic between $K_2O.4SiO_2$ and high quartz is at 764° and 72.0 weight per cent SiO_2, very near the $K_2O.4SiO_2$ composition. $K_2O.2SiO_2$ presents an unusual type of liquidus curve, and enters into solid solution with excess of both K_2O and SiO_2, the solid solutions decomposing into the pure compound and a melt at 814° and 993°, on the two sides of the composition of the compound. A reversible inversion is found in $K_2O.2SiO_2$ at 590°.

Geophysical Laboratory,
Carnegie Institution of Washington,
May, 1929.

THE VAPOR PRESSURES OF SULFUR BETWEEN 100° AND 550° WITH RELATED THERMAL DATA[*]

BY WILLIAM A. WEST AND ALAN W. C. MENZIES

No previous observer of the vapor pressures of sulfur has extended his measurements over a range of more than 200°, and only in two cases, (below 120° and from 390° to 445°), do the results of different observers overlap by more than one or two readings. In every case, marked divergence is found between the values of different observers, (see later tables), so that reliable knowledge of either the absolute value of the vapor pressure or of the shape of the curve, over any extended range, has been impossible. The only exception is the neighborhood of the boiling point, where much work has been done, which has been summarized by Mueller and Burgess,[1] with the adoption of 444.60° as the accepted value of the sulfur boiling point.

In an attempt to clear up this unsatisfactory situation, a series of measurements has been made extending from 104° to 543°, over a pressure range of 250,000-fold. An equation has been computed which appears adequately to represent the vapor pressure curve over this range. From this equation the related thermal data have been calculated.

I. Experimental Methods

A. *Thermometry.*

Temperatures were measured by means of a platinum resistance thermometer, of the compensating lead type, wound on mica, with a "Vitreosil" opaque-silica protecting tube. It was calibrated against the freezing and boiling points of water, and the melting point of zinc. The first two were determined in the usual way, and the last by using Melting Point Zinc, No. 43b, as supplied by the Bureau of Standards, the given melting point being 419.43°. Difficulty was at first experienced in obtaining consistent results with the ice point, due to soluble material persistently remaining in the pores of the silica tube. It was found that this could be remedied by steaming out in the boiling flask for one hour, after which constant and consistent results were always obtained. A tube of transparent quartz would have obviated this difficulty.

Resistances were measured by means of a Mueller Type Thermometer Bridge, made by Leeds and Northrup. The makers supplied calibration data showing no deviations which would affect our results. We checked the various resistances of the bridge against each other, and found no discrepancies worth taking into account. For temperatures above the range of the

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[*] Presented at the Am. Chem. Soc. meeting, Columbus, Ohio, April 1929. This paper constitutes a portion of the doctorate thesis submitted by William A. West to the Faculty of Princeton University.

[1] Scientific Paper, Bureau of Standards, No. 339 (1919).

bridge, (260°, for our thermometer), a supplementary resistance was used, whose value was determined before and after each series of observations.

An e.m.f. of 2 volts was used in the bridge circuit, which gave an amperage through the thermometer well below that at which objectionable heating might occur.[1] The galvanometer was of such sensitivity that a change of resistance corresponding to 0.002° gave a perceptible deflection. The thermometer head was enclosed in a wooden box, and no thermal e.m.f. amounting to as much as 0.01° in the measurement was observed, although a reversing switch was used throughout.

The fixed points, and the constants of the Callendar formula, which were determined every two weeks, showed the usual slow progressive change, (see Mueller and Burgess: loc. cit.), but this was very small in amount. The following values were obtained at the beginning and end of the work:

	Jan. 7	Mar. 12
F.P. water	25.990 ohm	25.983 ohm
B.P. water	35.996 "	35.987 "
F.P. zinc	65.929 "	65.926 "
F.I.	10.006 "	10.004 "
δ	1.511	1.505

As already stated, the accepted value of the S.B.P. is 444.60°. Four observations were made near the boiling point, and were reduced to 760 mm by the Mueller and Burgess formula.[2] The value obtained was 444.57° ± .01, which agreement gives confidence in the calibration of the thermometric instruments.

B. *Vapor Pressure Measurement*

1. By the static isoteniscope method. This instrument and its use have been described by Smith and Menzies.[3] It was used for all pressures above 6 mm, and for a few below. From 20 to 1200 mm the pressures were measured by a closed mercury gauge, exhausted to below 0.01 mm. For pressures above 1200 mm the gauge was open to the air, the barometric pressure being given by a barometer previously corrected by comparison with the gauge readings. The arrangement of the apparatus and the determinations of corrections were similar to those described by Smith and Menzies (loc. cit.), except that a steel bar was used for the gauge scale, instead of a tape.

Pressures below 20 mm were measured by a McLeod gauge, the following procedure being used. The pressure was adjusted to the desired value, and then the temperature of the bath was changed a few hundredths of a degree at a time, till the liquid in the limbs of the isoteniscope became level, and remained so for at least 5 min. The viscosity of sulfur at this temperature, (210°–250°), is such that even this procedure cannot give results of

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[1] Mueller and Burgess: Bull. Bur. of Standards, 6, No. 2.

[2] Scientific paper, Bureau of Standards, No. 339 (1919).

[3] J. Am. Chem. Soc., 32, 1419 (1910).

high precision, at least at the lower end of the range. Nevertheless, measurements were made, to serve as an approximate check on the method next described.

2. By the vaporization bulb method. This method has been previously used by Menzies.[1] The form of apparatus finally adopted for use with sulfur is shown in Fig. 1. The 250 cc bulb A contained several grams of sulfur. It was repeatedly boiled out, and pure, dry nitrogen was admitted and pumped out to remove foreign gases. The measurement was then made as described by Menzies.

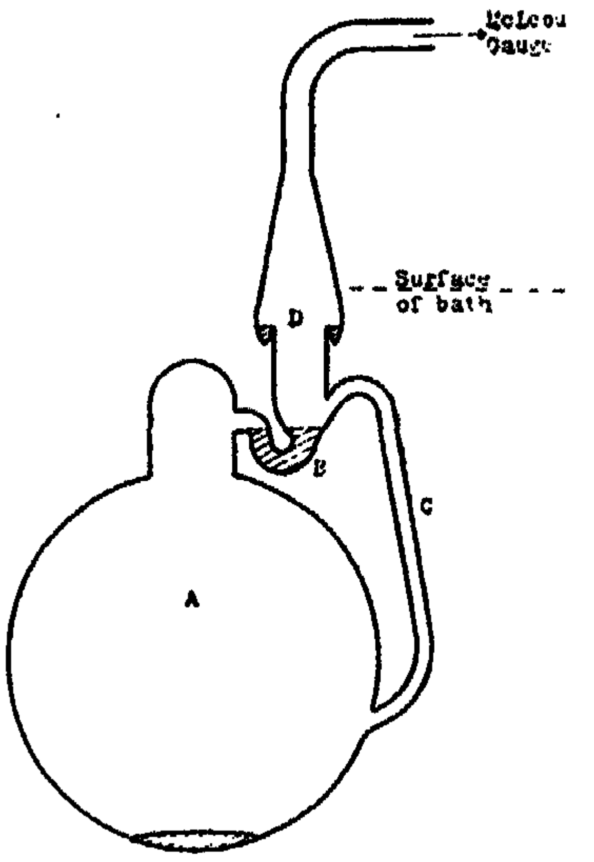

FIG. 1

This method is based on the following assumptions:

i. That the inert gas is not appreciably soluble in liquid sulfur. This was tested for by using different quantities of sulfur and pressures of nitrogen, and no indication of measurable solubility was found.

ii. That the bulb is filled with sulfur at saturation pressure. Preliminary experiments with a straight tube instead of the trap B, showed this not to be the case. A falling off at higher pressures was always observed. This appeared to be due to inability of the sulfur in the bottom of the bulb to maintain saturation pressure, while rapid diffusion was going on to the condensing surface in the tube. This effect is especially marked in the case of sulfur, since the high viscosity prevents running back of the liquid, down the tube and the sides of the bulb. The trap, and the small-bore connecting tube C, overcame this difficulty, since the extreme slowness of diffusion through tube C insured complete saturation in the bulb.

iii. That the pressure is the same throughout the system. A slight falling off at high vapor pressures was still observed (not more than 0.1 mm). This was thought to be due to back pressure caused by the rapid movement of sulfur vapor in the tube, from above the trap to the condensing surface. This would result in a relative lowering of pressure in the gauge part of the system. To remedy this the enlargement D was introduced, with an annular depression to hold sulfur. This was intended to reduce to a minimum the movement of sulfur vapor, by providing a source quite close to the condensing surface.

The guarantee that the sources of error have been overcome, is the agreement of the highest pressures so measured with the mean of those observed by the isoteniscope at the same temperatures. At lower vapor pressures the

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[1] J. Am. Chem. Soc., 42, 2218 (1920).

effects would, in any case, be much less. Also, overlapping ranges of pressures, measured with different pressures of nitrogen, were found in substantial agreement. (See later tables.)

Three McLeod gauges, of different capacities, were used, in order to obtain the maximum sensitivity for each range of pressures.

C. *Temperature Regulation.*

For the vaporization bulb method, an oil bath of 4 liter capacity was used; for the isoteniscope, a nitrate bath,[1] the container being a 2 liter beaker in an asbestos jacket, covered with a double thickness of asbestos board. Violent stirring was provided in each case. The temperature was regulated by adjusting one or more gas burners; with the nitrate bath, control was possible to within 0.01°, but with the oil bath the uncertainty was somewhat higher, though still well within the accuracy of pressure measurements. Lack of uniformity of bath temperature was tested for by making observations with the thermometer at different depths, and identical results were obtained. It may be noted that above 500° the nitrate bath quite appreciably attacks Pyrex.

D. *Purity of Material.*

Commerical roll sulfur was purified by fractional distillation followed by four complete distillations, in vacuo for one sample, in nitrogen at atmospheric pressure for another. It is well known that black spots continue to appear in sulfur, even after several distillations. This discoloration was observable in the material distilled in vacuo, but almost entirely absent in that done in nitrogen, perhaps because the higher temperature more completely and rapidly decomposed the organic matter responsible. Both samples gave identical vapor pressure results.

Mueller and Burgess (loc. cit.) have found that commercial sulfur gives a boiling point almost identical with that of the purified material. We tested this by the static method with the following result.

Isoteniscope filled with commercial roll sulfur. Boiling points (reduced to 760 mm) are given.

1.	After brief boiling out	444.44
2.	" " " "	444.47
3.	" " " "	444.51
4.	" thorough " "	444.56
5.	" " " "	444.57
6.	" standing 10 min.	444.44
7.	" thorough boiling out	444.56

When freshly boiled out, roll sulfur yields a value identical with that for purified sulfur, but on standing, volatile matter seems to appear, which slightly lowers the observed boiling point. Nothing of this sort was observed with the purified sulfur. The effect may be due to the decomposition of the

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[1] Menzies and Dutt: J. Am. Chem. Soc., 33, 1366 (1911).

organic matter present, or to the formation of a small amount of CS_2. This slow liberation of volatile matter would, of course, be entirely negligible in its effect on the dynamically determined boiling point.

II. Results

A. *Our own results.*

Our results are tabulated in the first two columns of Table I. In the column headed Method, "B" indicates vaporization bulb, the number following designating the series: "B1" with the most sensitive McLeod gauge,

TABLE I

Our Results (mm of mercury)

No.	Temp. °C	p. obs.	p. calc.	diff.	percent	method
1	103.48	0.011	0.0092	+.0018	+19.5	B1
2	115.88	0.026	0.0228	+.0032	+14.0	B2
3	117.03	0.023	0.0247	−.0017	− 6.9	B1
4	123.30	0.040	0.0378	+.0022	+ 5.8	B1
5	134.44	0.076	0.0776	−.0016	− 2.1	B2
6	152.30	0.218	0.220	−.002	− 0.9	B2
7	156.16	0.28	0.271	+.009	+ 3.3	B3
8	172.90	0.630	0.636	−.006	− 0.9	B2
9	175.68	0.72	0.724	−.004	− 0.6	B3
10	196.90	1.94	1.86	+.02	+ 1.1	B3
11	213.20	3.72	3.57	+.15	+ 4.2	Is_1
12	214.20	3.83	3.71	+.12	+ 3.2	Is_1
13	219.94	4.56	4.60	−.04	− 0.9	B3
14	223.74	5.20	5.27	−.07	− 1.3	Is_1
15	227.45	6.30	6.01	+.29	+ 4.8	Is_1
16	227.59	5.94	6.04	−.10	− 1.7	B3
17	246.84	11.80	11.48	+.32	+ 2.8	Is_1
18	251.37	13.02	13.22	−.20	− 1.5	Is_1
19	271.12	23.80	23.65	+.15	+ 0.6	Is(5)
20	298.64	48.7	48.79	−.09	− 0.2	Is
21	328.54	97.40	97.71	−.31	− 0.3	Is(7)
22	364.40	202.1	201.6	+.5	+ 0.2	Is(2)
23	387.55	307.5	306.8	+.7	+ 0.2	Is
24	413.09	470.5	470.2	+.3	+ 0.1	Is
25	444.57	760.0	760.0	—	—	Is(4)
26	467.33	1045.2	1047.2	−2.0	− 0.2	Is
27	478.78	1225.8	1228.3	−2.5	− 0.2	Is
28	483.01	1286.6	1293.5	−6.9	− 0.5	Is
29	487.23	1354.7	1363.9	−9.2	− 0.7	Is
30	490.73	1416.0	1422.6	−6.6	− 0.4	Is
31	503.95	1675.3	1680.2	−4.9	− 0.3	Is
32	543.08	2689.2	2675.2	+14.0	+ 0.5	Is

nitrogen pressure at room temperature 0.184 mm; "B_2," the intermediate gauge, nitrogen pressure 0.378 mm; "B_3" the least sensitive gauge, nitrogen pressure 1.96 mm. "Is" indicates isoteniscope and mercury gauge; "Is_1," isoteniscope and McLeod gauge. The numbers following Nos. 19, 21, 22, and 25, indicate that the result given is the mean of such number of observations, taken very close together. No. 25 is reduced to 760 mm by the Mueller and Burgess formula.

TABLE II

Vapor Pressures of Sulfur calculated from Our Equation

Temp. °C	p (mm Hg)	Temp. °C	p (mm Hg)	Temp. °C	p (mm Hg
120	0.030_4	270	$22._9$	420	$524._4$
130	0.058_7	280	$30._2$	430	$612._1$
140	0.10_9	290	$39._3$	440	$710._7$
150	0.19_4	300	$50._4$	450	$822._1$
160	0.33_2	310	$64._1$	460	$946._5$
170	0.55_2	320	$80._7$	470	108_6
180	0.88_8	330	$100._6$	480	124_1
190	1.3_9	340	$124._3$	490	141_4
200	2.1_2	350	$152._5$	500	160_5
210	3.1_6	360	$185._4$	510	181_5
220	4.6_0	370	$223._9$	520	204_8
230	6.5_6	380	$268._5$	530	230_3
240	9.1_9	390	$320._2$	540	258_3
250	$12._7$	400	$379._5$	550	287_0
260	$17._2$	410	$447._2$		

It was found impossible to represent these observations by a 3 or 4 constant formula of the type derived from the Clapeyron-Clausius equation, which is not surprising, considering the complexity of the liquid and vapor involved. Recourse was then had to Biot's equation, with which a satisfactory fit was obtained. Columns 3, 4, and 5 give, respectively, the corresponding pressures calculated from this equation, and the absolute and percentage deviations of the observed values from those calculated.

Biot's equation: $\log p = a + b^{\alpha t} + c^{\beta t}$

$a = 6.109689$ $\log \alpha = \bar{1}.9992626992$

$\log b = 1.0229544$ (neg.) $\log \beta = \bar{1}.9959962 84$

$\log c = 1.9198970$ (neg.)

Between 270° and 550° the agreement is to within a few tenths of one percent. It seems probable that an even better fit could be obtained by using a special equation for this limited range only, but at best the gain would be small, and is outweighed by the advantages of a single equation for the whole range. Below 270° the mean deviation rises, and is over 2 percent from 210° to 270°; it is about 1 percent from 120° to 210°. The curve, then, is simply the smoothed mean of a considerable number of observations. Below 120° the curve is an approximate exterpolation, since the error of measurement alone is quite high, and the occurrence of the melting point would mark a discontinuity.

Table II gives the vapor pressures for every ten degrees from 120° to 550°, as calculated from our equation.

B. *Results of Others.*

The results of other observers between these temperatures are listed in Table III, with corresponding pressures calculated from our equation, and deviations from the same. G indicates Gruener;[1] R and G, Ruff and Graf;[2] M, Matthies;[3] B, Bodenstein;[4] R, Regnault.[5]

Table III

Results of Others

Obs.	Temp. °C	p obs.	p calc.		diff.	percent
R and G	104.0	0.0115	0.0096	+	.0019	+19.8
G	104.4	0.0100	0.0103	−	.0003	− 3.0
G	109.8	0.0134	0.0137	−	.0003	− 2.2
R and G	110.8	0.0200	0.0159	+	.0041	+25.8
R and G	114.5	0.0285	0.0207	+	.0072	+34.7
G	120.5	0.0351	0.0314	+	.0037	+11.8
R and G	123.8	0.0535	0.0381	+	.0154	+40.0
R and G	131.9	0.081	0.0622	+	.0188	+30.3
R and G	132.2	0.079	0.0674	+	.0116	+17.2
R and G	133.1	0.088	0.0714	+	.0166	+23.2
R and G	141.0	0.131	0.115	+	.016	+13.9
R and G	147.0	0.192	0.162	+	.030	+18.5
R and G	157.0	0.332	0.284	+	.048	+16.9
R and G	162.0	0.403	0.359	+	.044	+12.2
R and G	172.0	0.629	0.608	+	.021	+ 3.5
R and G	189.5	1.38	1.36	+	.02	+ 1.5
R and G	211.3	3.14	3.32	−	.18	− 5.5
M	241.8	8.45	9.75	−	1.30	−13.2
M	265.0	20.5	19.9	+	.6	+ 3.0
M	306.5	53.5	59.0	−	5.5	− 9.3
M	341.7	105.5	128.8	−	23.3	−17.9
M	352.5	133.0	160.5	−	30.5	−18.7
M	363.0	176.0	196.3	−	20.3	−10.2
B	374	240	240.9	−	.9	− 0.5

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[1] J. Am. Chem. Soc., 29, 1395 (1907).

[2] Z. anorg. Chem., 58, 209 (1908).

[3] Physik. Z., 7, 395 (1906).

[4] Z. physik. Chem., 20, 113 (1899).

[5] Mém. de l'Acad., 26, 339 (1862).

TABLE III (continued)

Obs.	Temp. °C	p obs.	p calc.	diff.	percent
M	379.4	250.1	265.7	− 15.6	− 5.9
R	390	272.3	320.2	− 47.9	−14.9
B	393	336	340.3	− 3.7	− 1.1
R	400	329.0	379.5	− 50.5	−13.2
R	410	395.2	447.2	− 52.0	−11.6
B	410	443	450.7	− 6.3	− 1.4
R	420	472.1	524.4	− 52.3	−10.0
B	427	580	584.7	− 4.7	− 0.8
R	430	561.0	612.1	− 51.1	− 8.2
R	440	663.1	710.7	− 47.6	− 6.7
B	444.53	760	759.5	+ .5	+ 0.1
R	450	779.9	822.1	− 42.2	− 5.1
R	460	912.7	946.5	− 32.8	− 3.5
R	470	1063	1086	− 23	− 2.0
R	480	1232	1241	− 8	− 0.7
R	490	1423	1414	+ 9	+ 0.6
R	500	1635	1605	+ 30	+ 1.9
R	510	1872	1815	+ 57	+ 3.1
R	520	2133	2048	+ 85	+ 4.1
R	530	2422	2303	+119	+ 5.2
R	540	2739	2583	+156	+ 6.0

(Regnault's results are given here only to four figures).

Gruener, and Ruff and Graf used the gas current saturation method, assuming sulfur vapor to be S_8. Preuner and Schupp[1] have since shown that the vapor density of sulfur is less than this, even at 100°. The correction, based on their data, would range from 3 percent at 105° to 6 percent at 210°. If this correction be made, it is seen that the highest observation of Ruff and Graf falls almost exactly on our curve, but that their other results are increasingly high as we come down the temperature scale. Gruener's two lower values also fall on our curve, when corrected, but his highest one is above it. This last is the most uncertain, according to Gruener, who states that his apparatus was not well adapted to higher temperatures. It may be noted that Gruener's results below 100° fall consistently lower than those of Ruff and Graf, and the latter explain this discrepancy by criticism of details of Gruener's technique. It is striking that Ruff and Graf agree with us at the higher pressures, where, as has been pointed out, systematic error would be most likely to make our results low.

Matthies employed the boiling point method, measuring pressures with a manometer or a McLeod gauge, and temperatures with a thermocouple. His results below 240° are omitted, since he considers that they are somewhat doubtful; they fall increasingly lower than our curve. With one exception,

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[1] Z. physik. Chem., 68, 129 (1909).

his observations lie below our curve. It can be understood that at these low pressures, with a liquid of the viscosity of sulfur, the boiling point method presents considerable difficulty. He does not give details of the method of heating, nor of precautions to prevent superheating.

The results of Bodenstein show very good agreement with our curve; considering that he gives his temperatures only to the nearest degree, the agreement is practically within his experimental error.

In view of the advances in technique which have taken place since the time of Regnault, the comparison of his results serves to confirm the high opinion in which his work has always been held.

A futher comparison with previous measurements may be obtained near the boiling point. Mueller and Burgess (loc. cit.) have shown that for several degrees on either side of the boiling point the temperature may be computed from the equation:

$$t = t_{760} + 0.0910(p-760) - 0.000049(p-760)^2$$

If we assume $t_{760} = 444.57°$, and calculate points on either side of the normal boiling point, we obtain the following results for the two equations:

pressure	M and B	Ours	Dev. (°C)
793.86	447.590	447.570	−.020
706.46	439.543	439.570	+.027

This small deviation is in the same direction, and of the same order of magnitude, as the slight lack of fit already referred to; *i.e.* our calculated curve similarly crosses our observational curve at a very small angle, at the boiling point.

In conclusion, it appears that the most serious divergence from our curve, of observations made under favorable conditions, is that of the results of Ruff and Graf. Gruener, using the same method as they did, likewise obtained lower results, in consonance with our own findings.

C. *Accuracy of Our Results.*

The maximum absolute error in temperature measurement we estimate as 0.05°. Above 400° this is the principal source of uncertainty in the results; below 300° it is entirely negligible, compared to errors in pressure measurement. Pressures measured with isoteniscope and mercury gauge may be in error by not more than 0.3 mm above 300°, and rather more, below, due to difficulty in levelling. For lower pressures, measured with the McLeod gauge, the error is 0.1 – 0.2 mm, due almost entirely to uncertainty in levelling the isoteniscope. In the vaporization bulb method, apart from possible systematic error, the uncertainty is about 1 percent, except at the lowest pressures, where it is higher.

The following summary may be made:

Temp. range	Estimated mean error of observation (percent of pressure)
100°—120°	10 percent
120—210	1
210—260	2.5
260—300	1
300—350	0.3
350—475	0.1
475—550	0.2

III. Related Thermal Data

A. *Heat of Vaporization.*

Having obtained a reasonably good equation for the vapor pressure curve of sulfur, we may calculate the latent heat of vaporization from the Clapeyron-Clausius equation:

$$L = T(v_g - v_l)(dp/dt)$$

dp/dt is obtained by differentiating Biot's equation. v_g may be found from the vapor density data of Preuner and Schupp, (loc. cit.), while v_l is appreciable, relatively to v_g, only at the extreme upper end of the curve. The first two columns of Table IV give temperatures and corresponding heats of vaporization in cal/g. The same values are shown graphically by the solid curve in Fig. 2(A).

It is seen that L diminishes rapidly to a minimum at about 365°, and then rises. The general rule for normal substances is that L should diminish continuously, becoming zero at the critical temperature. Some substances, which are associated in the liquid phase, show a maximum at some temperature, (e.g. acetic acid[1]), but for a liquid to show a minimum heat of vaporization is unusual. The explanation appears to be given by the results of Preuner and Schupp (loc. cit.) They calculate the relative quantities of different molecules in the saturated vapor at different temperatures, and show that S_2 does not begin to appear till above 300°, and then only in small amount. However, they show from equilibrium considerations that $S_8 \longrightarrow 4S_2$ requires about 370 cal/g, while we see that $S_{liq} \longrightarrow S_{vap}$, at these temperatures, requires only 70—80 cal/g. If we calculate the amount of energy needed to form the percentage of S_2 given by Preuner and Schupp, and subtract it, at each temperature, from our heats of vaporization, we obtain the values in column 3 of Table IV, and the dotted curve in Fig. 2 (A). It appears that the abnormal rise is caused entirely by this dissociation in the vapor phase, and the fact that the "corrected" curve follows the normal course seems to confirm Preuner and Schupp's reasoning.

By interpolation for the normal boiling point we obtain the value of L = 69.5 cal/g. This may be compared with two recent determinations. Beck-

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[1] Ramsay and Young: J. Chem. Soc., 49, 790 (1886).

mann and Liesche[1] obtained the ebullioscopic constant and heat of vaporization of sulfur from vapor pressure data by Bodenstein, and found the value 64.8 cal/g. They assumed the molecular weight to be identical in liquid and vapor, namely 230.6. If we use 214, the value of Preuner and Schupp,

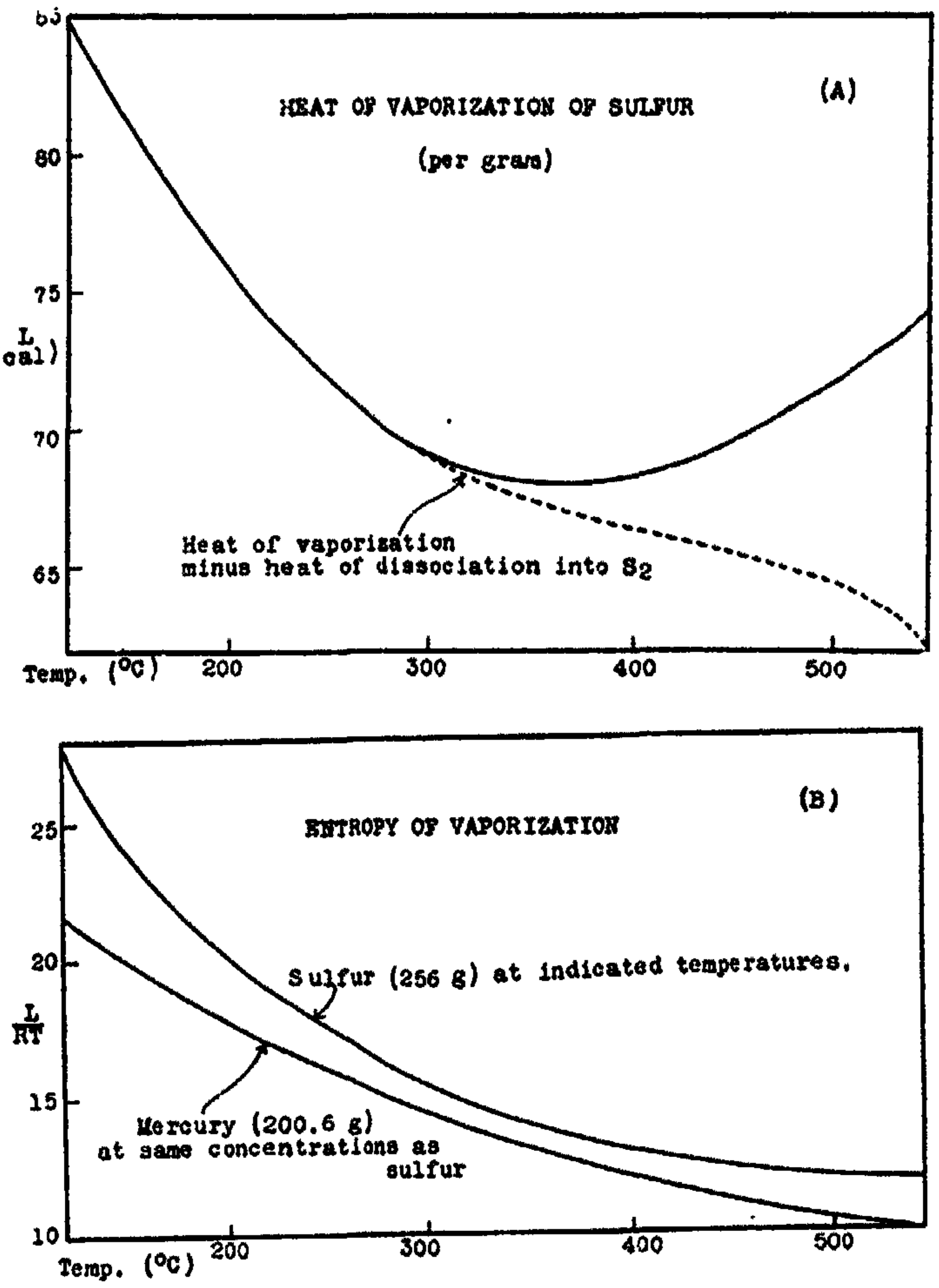

FIG. 2

we obtain, by their method, 71.3 cal/g. It will be shown later that the molecular weights of liquid and vapor are probably not very different at these temperatures. Awberry[2] determined the heat of vaporization of sulfur at the boiling point calorimetrically, and found 79 cal/g, with an estimated error of 2 percent.

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[1] Z. anorg. Chem., 85, 31 (1914).

[2] Proc. Phys. Soc. London, 39, 417 (1927).

TABLE IV

Heat of Vaporization of sulfur

Temp. °C	L (cal/g)	L minus heat of dissociation to S_2 present in vapor	Temp. °C	L(cal/g)	L minus heat of dissociation to S_2 present in vapor
120	84.8		320	68.6	68.3
140	82.4		340	68.2	67.7
160	79.7		360	68.1	67.2
180	77.5		380	68.2	66.8
200	73.7		400	68.4	66.4
220	75.5		420	68.7	66.0
240	72.3		440	69.3	65.6
260	71.0		460	70.0	65.2
280	70.0		480	70.9	64.9
300	69.1		500	71.8	64.1
			520	72.9	63.6
			540	73.9	62.7

The accuracy of our figure depends on the values of dp/dt and the vapor density. We may obtain the former by differentiating the equation of Mueller and Burgess, (loc. cit) and find thereby $L = 69.6$, instead of 69.5 as computed from our equation. For the latter we have to depend on Preuner and Schupp, and there seems to be no reason for suspecting any error in their work at all approaching our lack of agreement with Awberry.

B. *Entropy of Vaporization.*

Hildebrand[1] has shown that, for normal liquids, molar entropies of vaporization are approximately equal at equal concentrations of saturated vapor. In particular, for a vapor concentration where $\log T - \log p = 0.500$, $L/RT = 13.7$ for normal liquids, while for associated liquids the value is decidedly higher. Sulfur attains this concentration at 364.5°, and at this temperature $L/RT = 13.6$, which would indicate that the molecular constitution of liquid and vapor are the same. If we compute the entropy of vaporization over the whole temperature range, a different conclusion is reached. Fig. II (B) shows graphically L/RT for 256g of sulfur, plotted against temperature, with a similar curve for mercury at corresponding concentrations. Mercury is chosen because accurate vapor pressure data are available;[2] Hildebrand has shown that, in common with other metals, it gives entropies of vaporization which are lower than those of "normal" liquids, such as hydrocarbons.

It is seen that the curve for sulfur rises at each end. At high temperatures, this is due to the formation of S_2 in the vapor, the liquid being relatively associated by contrast. At low temperatures the vapor is essentially S_8, and yet the high entropy of vaporization indicates marked association in the

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[1] J. Am. Chem. Soc., 37, 970 (1915).

[2] Menzies: Z. physik. Chem., 130, 90 (1927).

liquid. This would call for a polymerized molecule, perhaps $(S_8)_2$, which dissociated rapidly with rise in temperature. Molecular weight determinations of sulfur in other solvents practically all give S_8, but partition experiments show that where different molecular forms are possible, a particular solvent usually dissolves only one type. Since the solvents used for sulfur have all been of one class, namely organic compounds, it appears that molecular weight data do not furnish a valid objection to the hypothesis stated above. Equally satisfactory would be the theory that there are different forms of S_8 molecules, possessing different quantities of energy. It is of interest to note that X-ray measurements of the lattice of rhombic sulfur[1] indicate that the crystal molecule may consist of 16 atoms.

Summary

1. Experimental determinations of the vapor pressure of sulfur have been made from 104° to 543°.

2. Constants have been calculated for an empirical equation which adequately represents these observations, and from it has been constructed a table of vapor pressures for each ten degrees, over this range. The results of other workers are compared with those given by this equation.

3. The heats of vaporization and entropies of vaporization have been calculated over this temperature range. Their abnormalities have been discussed in relation to the molecular constitution of liquid and vapor.

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[1] Mark and Wigner: Z. physik. Chem., **111**, 398 (1924).

THE RATE OF ATTAINMENT OF VAPOR PRESSURE EQUILIBRIUM IN LIQUIDS[*]

BY WILLIAM A. WEST AND ALAN W. C. MENZIES

In his presidential address to the London Chemical Society in 1927, H. B. Baker[1] reported that the vapor pressures, measured at room temperature, of certain undried liquids were appreciably raised by previous prolonged treatment at high temperatures. He considered that this was due to a delay in attainment of internal equilibrium. This would be similar to the well-known results of heat treatment of metals. It seemed to be desirable to investigate this phenomenon more fully, since, if it were so, vapor pressure of a liquid would be a function of time of heating, previous treatment of material, etc. Consistent vapor pressure measurements could then be obtained only by following a standardized procedure, based on observations of the rate of attainment of equilibrium in the liquid in question.

A. *Method.*

We used two isoteniscopes,[2] which were dried, filled with samples of the same liquid, and then boiled out in a bath near room temperature till they showed identical pressures. One was then closed, either by sealing off or with a mercury seal, and heated for some time in an oven or a glycerine bath. It was then brought back to the original bath, opened, and the vapor pressure compared with that of the unheated one. (In the case of liquid sulfur a different procedure was employed, as described later).

The sensitivity of the method was from 7 to 15 times that of one employing a mercury column for pressure measurements, according to the density of the liquid used. Baker made use of the classical barometer tube method.

B. *Liquids Investigated.*

1. Normal behavior expected.

Benzene, purified and dried over sodium. This is generally considered to be a normal liquid, except perhaps when intensively desiccated.[3]

Water. Although this is believed to have an internal equilibrium between different molecular forms, this equilibrium is attained practically instantaneously. Baker obtained a negative result by his method.

2. Abnormal behavior possible.

Acetone.

Ethyl alcohol, absolute.

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[*] Presented at the Am. Chem. Soc. meeting, Swampscott, Mass., Sept. 1928. This paper constitutes a portion of the doctorate thesis submitted by William A. West to the Faculty of Princeton University.

[1] J. Chem. Soc., 1927, 951.

[2] Smith and Menzies: J. Am. Chem. Soc., 41, 1419 (1910).

[3] Baker: J. Chem. Soc., 1922, 570.

Acetic acid, M.P. 16.6°, B.P. 117.8°. The material had been subjected to fractional crystallization till the melting point became constant within 0.02°, and was then distilled twice within a range of 0.02°.

These three, having respectively carbonyl, hydroxyl, and carboxyl groups, might be expected to show molecular association, and therefore an internal equilibrium which might not be very rapidly attained. Acetic acid undoubtedly does have such an internal equilibrium, and it was reported by Baker to show a marked lag in attainment of vapor pressure equilibrium.

3. Abnormal behavior probable.

Liquid sulfur. The evidence for the existence of an internal equilibrium is well-known. Also, the extremely high viscosity[1] over the temperature range 160°–250° would seem to favor a retardation of equilibrium attainment.

In all cases where the material was distilled at least a week was allowed to pass before using it, to permit equilibrium at the lower temperature to become established.

C. *Results.*

1. Tabulation of results for the first five liquids.

	1	2	3	4	5	6	7
Benzene	18	120	25	6	0	sealed	oven
Water	6	119	35	10	−1	"	"
Acetone	23	120	25	5	0	"	"
Alcohol	19	113	20	8	0	Hg seal	Glycerine bath
Acetic acid	18	145	20	4	0	" "	" "
Acetic acid	20	140	20	5	0	" "	" "

Column 1: time of heating. (hours).
2: temperature to which heated. (°C)
3: temperature of comparison bath. (°C)
4: time between removal from heating and first reading (min.)
5: increase in v. p. of heated isoteniscope. (in mm of liquid used)
6: method of closing isoteniscope.
7: method of heating.

No increase in vapor pressure was observed. In the case of water the slight lowering is thought to be due to its having dissolved material from the glass.

2. Liquid sulfur.

After boiling out at a higher temperature the isoteniscopes were brought to 215°, a nitrate bath being used. One was then raised into a glass cylinder kept at 150°. It is well known that the dark red, viscous form of sulfur becomes pale yellow and mobile when cooled below about 160°. After giving ample time for this change to take place, the isoteniscope was lowered

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[1] Farr and McLeod: Proc. Roy. Soc., 97, 80 (1920).

again into the bath, and compared with the one which had remained there. Thus the sulfur would change to the viscous form, rise in temperature through the range of greatest viscosity, and finally come to equilibrium where the viscosity was not much below the maximum.

A mixture of sodium and potassium thiocyanates was used as a confining liquid in the isoteniscope. This was liquid at 140°, and provided a non-objectionable, mobile, confining fluid.

Two observations were made:

Temp. of bath	215
Temp. of cylinder	150
Time in cylinder	45 min.

In each case, the vapor pressure of the previously cooled isoteniscope rose slowly, till, in about 4 min., it became equal to that of the comparison instrument. It is considered that this shows no delay in attainment of vapor pressure equilibrium at all distinguishable from the ordinary lag in thermal equilibrium.

D. *Explanation of Baker's Result for Acetic Acid.*

During this investigation, work in this laboratory by Dr. Sydney L. Wright (to be published), showed that the acetic acid used by us could be divided into fractions whose vapor pressures differed by as much as 4 mm of mercury at the boiling point, by very slow isothermal distillation in a special form of apparatus. This was undoubtedly due to its water content, in spite of its having been twice distilled within a range of 0.02°. Since Baker mentions no special precautions in purifying his material, we feel justified in assuming that it was not superior to ours.

When Baker's barometer tube containing acetic acid above the mercury was placed in the heated bath, the vapor at equilibrium with the liquid would contain a larger proportion of the more volatile constituent. When cooled, this vapor would largely condense, forming a more volatile layer on the surface of the meniscus, and therefore increasing the observed vapor pressure. On standing, diffusion in the liquid would eventually bring the vapor pressure back to normal.

An instrument was designed to test this explanation. (see cut). The bulb C was filled with acetic acid and thoroughly boiled out, being held in an inclined position. Stopcock G was then closed and the instrument brought back to the vertical, so that the liquid was all driven into bulbs B and E and the connecting tubes, the only vapor being in bulb C. The right-hand part of the apparatus was placed in a bath at 20°, the column of liquid was adjusted to a marked point A by changing the quantity of mercury in bulb E, and the reading of the mercury manometer D taken. After heating in a glycerine bath at 80° for 18 hours, the instrument was brought back to the bath at 20°, care being taken not to permit large or sudden movements of the meniscus during cooling. The manometer was read again, then the liquid from bulb B was allowed to rise into C, gently agitated, drawn down again to A, and the manometer read a third time. This was done with the acetic acid previously used, and also with another sample of melting point 16.5°.

M.P. of acid	Change in pressure after heating 18 hr.	After mixing
16.5°	+4.0 mm Hg	Increase disappeared and v.p. returned to original value.
16.6°	+0.6 " "	

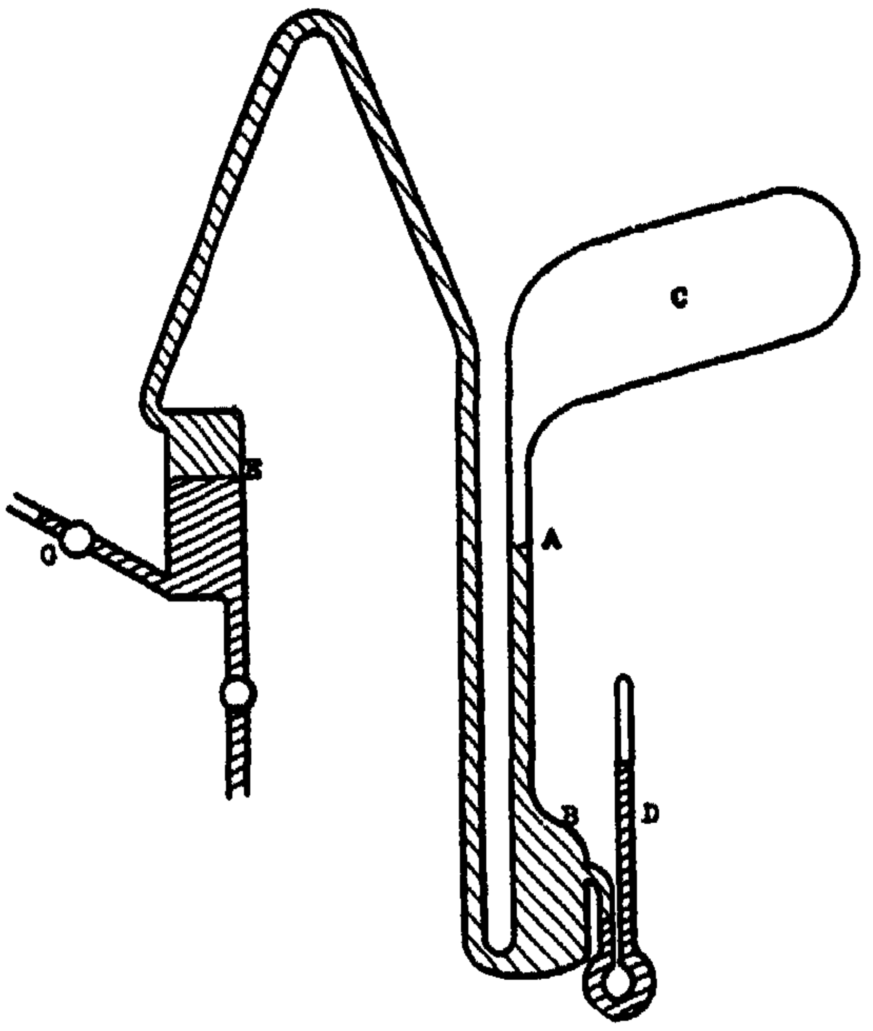

FIG. 1

Baker heated his material 24 hours at 80°, and found an increase in vapor pressure of 2 mm, which had disappeared one week later. There is of course no reason to expect quantitative agreement between our results and Baker's but the magnitude of the effect found appears to be about the same.

Summary

1. Six liquids, of different types, have been tested for delay in attainment of vapor pressure equilibrium with change in temperature. In five cases the comparison temperature was similar to that used by Baker.
2. The temperature of heating varied from 65° to 125° above the comparison temperature, and the limit of observable pressure difference averaged less than 0.05 mm of mercury.
3. In no case was a delay in vapor pressure equilibrium found which was distinguishable from the lag in thermal equilibrium.
4. An explanation is offered, supported by experimental evidence, for the result obtained by Baker for acetic acid.

SOME ASPECTS OF METABOLISM AND DEFICIENCY DISEASES AND THEIR TREATMENT BY LIGHT AND IRON PREPARATIONS

95t, 119

BY N. R. DHAR

In the previous papers[1] I have suggested that pernicious anaemia, cancer of the tongue and stomach, leukaemia and Hodgkin's disease are likely to be deficiency diseases.

I have also shown that most deficiency diseases like scurvy, beri-beri, pellagra, malnutritional oedema, rickets, pernicious anaemia, etc., are associated with gastrointestinal disturbances. This fact supports my contention that deficiency diseases are caused mainly by the want of proper metabolism or oxidation of food materials through the lack of accelerators or promotors like vitamins, internal secretions, etc., which accelerate the oxidation of food materials by air in presence of oxidising enzymes in the body. I have also emphasised that sunlight ought to prove efficacious in deficiency and metabolism diseases. In this communication I shall adduce further evidences in favour of the above views and consider other aspects of deficiency diseases.

Epidemic Dropsy at Allahabad, India

In the last cold weather there were about two hundred cases of epidemic dropsy amongst the Bengali community of Allahabad (India). The staple food of these people is polished rice and fish curry cooked in mustard oil, and this community mainly consists of lower middle class people. A similar outbreak of epidemic dropsy occurred at Calcutta amongst the Bengalis in the months of September, October, and November 1926. Some people believed that owing to improper storing of rice, some kind of fungus grew on the rice which acted as a poison and caused the disease.

It should be remembered that this view regarding the origin of epidemic dropsy and beri-beri is more or less identical with the theory of the origin of pellagra advanced by Lombroso and Bellardini in 1871. These authors believed that pellagra was caused by the consumption of damaged maize either by damp or being insufficiently cured and in that state acts as a medium for the growth of poisonous fungi of different variety. There is another school of thought which believed that the occurrence of epidemic dropsy is due to a poison present in mustard oil; the mustard seed is supposed to contain another seed as an impurity similar to that occurring in lentil which causes lathyrism.

In order to test the above view, pigeons in our laboratories were fed on samples of suspected rice and oil but no indication of epidemic dropsy was detectable among these birds. From a critical examination of typical cases

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[1] Dhar: Chemie der Zelle und Gewebe, 12, 217, 225, 286 (1925); 13, 119, 209 (1926); J. Phys. Chem., 29, 376 (1925).

and the corresponding diet it appears that this attack of epidemic dropsy was due to malnutrition and want of vitamins aided by humidity and insanitary living conditions. There were no cases of epidemic dropsy in those families which were taking germinating grains and other seeds. It is interesting to note that the working classes in India who have more or less an outdoor life, and eat several raw things like onions, radishes, cucumbers, grains, maize, etc., do not suffer from deficiency and metabolism diseases, bad teeth, etc., as much as the lower middle classes who have to lead an indoor life because of their clerical and other indoor duties and do not get as much exercise and sunlight as the working classes do. Moreover, these lower middle class people cannot afford to have really good meals consisting of eggs, milk, meat, butter, fish, bread, etc. Unlike the working classes they can not stand raw things, due to indigestion and suffer constantly from metabolism and deficiency diseases.

It is remarkable that the Bengali community living at places like Agra, Cawnpore, and Lucknow, which are not far from Allahabad, under consitions similar to those living at Allahabad did not suffer from epidemic dropsy in the last cold weather.

Moreover, McCarrison[1] insists that beri-beri is not strictly a disease due to food deficiency. He says that in country districts about Madras the home pounding of rice is still the common practice and beri-beri occurs amongst the users of home-pounded or unpolished rice in endemic areas. McCarrison says that contrary to the usually accepted belief, Mahomedans in endemic areas of Madras Presidency suffer more from beri-beri than Hindus, notwithstanding that the food of the former is much more varied and that the latter restrict themselves much more rigidly to a rice dietary. It seems to me that the Hindus avoid beri-beri by the intake of leafy and other vegetables and sour milk preparations in the Madras Presidency. Another important fact which comes out clearly from observations on the origin of beri-beri and epidemic dropsy is that dampness of the surroundings and general uncleanliness of the people are the usual promoters of the disease. The view that beri-beri is a metabolism disease is suported by the observation of Okada and co-workers[2] that starvation of vitamin B leads to decrease of basal metabolism in human beings. In previous papers, I have advanced the view that vitamin B is an accelerator in the oxidation of carbohydrate food materials and that food materials rich in vitamin B should prove efficacious for diabetes and that pancreatic preparations should prove useful for beri-beri, which is likely to be caused by the break-down of carbohydrate metabolism.

Though Magnus-Levy[3] was unsuccessful in isolating an antidiabetic principle from oatmeal, Boruttau[4] found that the pancreas extracts, yeast,

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[1] Brit. Med. J., 1, 1924 I, 414.

[2] Japan Med. World, 3, 1923 III, 102.

[3] Spez. Path. Ther. inn. Krankh., 1 (1913).

[4] Biochem. Z., 88, 420 (1918).

and yeast extracts, inhibit the cleavage of glycogen in the isolated heart, while extracts from the peripheral oat layer decreases the sugar elimination in diabetic dog and in man. In India due to the richness of carbohydrates in normal diet, conditions set in which gradually lead to diabetes. These conditions strongly resemble the experimental glycosuria which has been described in pigeon beri-beri by Funk.[1]

Funk and von Schönborn[2] found that whereas in normal pigeons the glycogen and blood sugar content of the liver is 1.17% and 0.1% respectively, on an artificial vitamin-free diet the glycogen content drops to 0.48% and the blood sugar rises to 0.15%. Pigeon fed on an excess of sugar showed 4.5% glycogen and 0.15% blood sugar. On an excess of starch there is no glycogen and 0.26% blood sugar. In the last case if vitamin B is added the values for glycogen and blood sugar approach normal. These results were later repeated several times and corroborated by Funk.[3] The finding of glycosuria in pigeon beri-beri has not yet been confirmed in human beri-beri. Besides this Funk also studied the influence of substances having a known action on carbohydrate metabolism. Among them the effect of glucose, phlorizin, adrenaline, pituitrin thyroid, and parathyroid on pigeon beri-beri was tested on normal and rice-fed pigeons.

Of special interest was adrenaline, which shortened the life of the animal; this was also true of thyroid. The influence of parathyroid was quite different. While thyroid raised the blood sugar content of the liver, the addition of parathyroid increased the glycogen and aminoacid contents but had little effect on blood sugar. In a foregoing paper I have explained the occurrence of glycosuria on the addition of thyroid and adrenaline. The discovery of glycosuria in pigeon beri-beri may evidently be connected with some observations made by McCarrison.[4] He found that in avian beri-beri the suprarenals undergo considerable enlargement and are characterised by a high adrenaline content.

Influence of Light on Deficiency and Metabolism Diseases

In a recent communication[5] we have shown that the oxidation of carbohydrates, fats and nitrogenous substances by air at the ordinary temperature is markedly accelerated by sunlight. We are definitely of opinion that in presence of sunlight and artificial lights the metabolism in the animal body is increased and that is why light should prove efficacious in the treatment of rickets and other metabolism and deficiency diseases.

Sunlight has been found to be useful in the treatment of pernicious anaemia. Moreover rickets is practically unknown in tropical countries; though, due to poverty, the food supply of children in the tropics is quite

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[1] Z. physiol. Chem., 89, 378 (1914).

[2] J. Physiol., 48, 328 (1914).

[3] J. Physiol., 53, 247 (1919).

[4] Ind. J. Med. Research, 5, 2755 (1919).

[5] J. Phys. Chem., 32, 1263 (1927).

inadequate. People living in several parts of India take maize but there is very little pellagra in this country, few cases only were reported in Northern Behar. Some have regarded pellagra as the sunstroke of the skin. "Sun disease" was the old popular name of pellagra. We are, however, convinced that sunlight should be efficacious in the treatment of pellagra, because in presence of sunlight the metabolism of food materials in the animal body is increased. In Italy and other countries, pellagra is more frequent in the beginning of the spring. We are of opinion that this is due to the fact that in winter due to the shortage of vitamin in food stuffs and to the lack of sunshine, the animal body suffers from prepellagral conditions.

Ehrstrom[1] of Finland, in discussing spring tiredness and vitamin deficiency, states: "We are well in the Autumn after the light and open air in the Summer and we feel unwell in the Spring after the darkness of the Winter." Possibly the lack of vitamins in the winter diet and the absence of sunlight in winter caused the feeling of tiredness in beginning of the spring. A similar explanation holds good for the same feeling in the spring reported by the early settlers of America.

According to Appleton[2] the people of Labrador suffer constantly from deficiency diseases like beri-beri, oedema, scurvy, nightblindness, etc., because they are poor and cannot afford to have really good meals. Moreover, there is not much sunshine in Labrador.

According to Hoffman[3] cancer occurs more frequently in the cities than in the country and more among the well-to-do than among poor people. That this disease is associated with luxury consumption, is best recognisable from the statistical figures compiled during the war and from insurance statistics. It seems likely that sunlight is very efficacious in preventing cancer and that is why this disease is less frequent in tropical countries than in cooler ones.

Hart, Steenbock, Lepkovsky and Halpin[4] studied the effect of exposure to direct sunlight on the growth of chicks. They found that one half hour's exposure to direct sunlight was more potent in furnishing the antirachitic equivalent than was 5% of the synthetic ration fed as green clover. They fed two groups of chicks on the following diet: corn 97, sodium chloride 1, calcium chloride 2% and skimmed milk in excess. One group was fed white corn, the other group yellow corn. Both groups were exposed to sunlight daily. Those birds receiving the white corn which was low in vitamin A, did not respond to the sunlight treatment, whereas those receiving yellow corn and sunlight grew to be beautiful birds.

Hughes[5] found a condition to develop in chicks identical with rickets, when the birds are given satisfactory food but received sunlight filtered through glass. Chicks receiving the same food and treatment but expodes

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[1] Lancet, 1, 1924 I, 1278.

[2] Am. J. Pub. Health, 11, 617 (1921).

[3] Proc. 2nd Pan-Am. Sci. Congress, Washington, 10, 586 (1917).

[4] J. Biol. Chem., 58, 33 (1923).

[5] Science, 59, 213 (1924).

to direct sunlight for a few hours daily developed normally. He found ultraviolet light to have the same beneficial effect as direct sunlight.

Recently Huldschinsky[1] has used in tetany the sun ray therapy with which he was successful in the treatment of rickets.

Cramer and Drew[2] kept rats in darkness on a diet poor in vitamin A and found a slight diminution of blood platelets as compared with rats kept in a well lighted room on a similar diet. Exposure to the mercury vapour lamp increased the number of platelets to normal, and when anaemia was present increased the number of red cells. They conclude that light may be a stimulus to the formation of blood platelets but not an essential condition. The absence of light could be counteracted by an abundance of vitamin A.

Rennhard[3] reported experiments with diffused light and with direct sunlight, which showed clearly that development of yeast is more rapid in cultures exposed to direct sunlight. Ultraviolet rays are somewhat harmful in their action.

Hess, Unger and Pappenheimer[4] found that prolonged exposure to direct sunlight does not prevent scurvy in the guinea pigs. Gerstenberger and Burhams[5] found that scorbutic and polyneuritic infants and guinea pigs can burn carbohydrate completely. These results seem doubtful and the experiments should be repeated.

It seems certain from the foregoing results that sunlight and artificial lights are very favourable for growth and can stop rickets. Hence light plays the same role as that of vitamins A and D. We have proved experimentally that the slow oxidation of fat by air is accelerated by sunlight. Moreover, we have advanced the view that thyroid preparations should prove efficacious in the treatment of rickets, because thyroid secretion is likely to act as an accelerator in the oxidation of fat. Our experimental results on slow oxidation show that light acts as an accelerator in the oxidation of carbohydrates as well. Hence we believe that light should prove efficacious in the treatment of diabetes and beri-beri because both these diseases are due to disturbances of carbohydrate metabolism. Vitamin B and pancreatic preparations are likely to accelerate the oxidation of carbohydrates in the body and hence they should be beneficial towards diabetes, beri-beri and epidemic dropsy. Light is highly beneficial in the treatment of rickets and helps growth and hence light is likely to act as a more marked accelerator in the oxidation of fats than of carbohydrates. In other words, in presence of light the oxidation of fats is likely to be increased more than in the case of carbohydrates and that is why light is more efficacious towards rickets than towards diabetes, beri-beri and scurvy; but as we have proved experimentally that light can accelerate the oxidation of the three classes of food materials—carbohydrates,

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[1] Z. Kinderk., 26, 207 (1920).

[2] Brit. J. Expt. Path., 4, 271 (1923).

[3] Compt. rend. Soc. biol., 89, 1080 (1923).

[4] Proc. Soc. Exper. Biol. and Med., 19, 236 (1922).

[5] Proc. Am. Soc. Biol. Chem., 1922.

fats and proteins—we are convinced that light should prove efficacious towards deficiency and metabolism diseases like beri-beri, epidemic dropsy, scurvy, pellagra, diabetes, gout, etc.

Iron Preparations in Metabolism and Deficiency Diseases

In foregoing papers[1] I have emphasised the importance of iron preparations in the treatment of metabolism diseases. I have proved experimentally that the oxidation of tartaric acid, starch etc., by hydrogen peroxide is greatly accelerated by ferrous or ferric salts.

Moreover we[2] have shown that carbohydrates, fats and nitrogenous substances can be readily oxidised at the ordinary temperature by passing air in presence of ferrous hydroxide. Consequently we believe that deficiency and metabolism diseases like beri-beri, pellagra, scurvy, rickets, gout, diabetes, etc., should be amenable to treatment by iron preparations, because in presence of iron the oxidation of food materials will be accelerated.

McCollum and Simmonds[3] have shown that leafy vegetables are protective foods, because of their vitamin A content. We are however of opinion that the efficacy of the leafy vegetables is partly due to their iron contents. It has been found that in the absence of iron the higher plants fail to form chlorophyll, although iron is not actually contained in chlorophyll as it is present in haemoglobin. It is well known that iron is present in almost all green vegetables.

Defects of Bone Formation and Concentration of Hydrogen Ions in the Body

In a recent communication[4] I have discussed the formation of bones in the animal body and have shown that normal calcium phosphate existing in the serum in the colloidal state is adsorbed and precipitated by the cartilage as a solid. Similarly small amounts of calcium carbonate also exist in the colloidal state in the serum and this is also adsorbed and precipitated by the cartilage and thus normal ossification takes place. Moreover, it is well known that blood is slightly alkaline. If by any means there is a slight increase in the $H^{\cdot}$ ion concentration in the blood, the amount of calcium phosphate and calcium carbonate existing in the colloidal state will partly dissolve and hence their concentration will decrease and thus there will be disturbance of bone formation. It seems likely that in the body there is a definite equilibrium condition as represented by the following scheme:—

$$3\,Ca^{\cdot\cdot} + 2PO_4''' \rightleftarrows Ca_3(PO_4)_2 \text{ (Colloidal)} \rightleftarrows Ca_3(PO_4)_2 \text{ (Solid in bones)}$$

If the food lacks either in $Ca^{\cdot\cdot}$ or PO_4''' ions, bone formation cannot take place normally because the proper concentration of calcium phosphate in the colloidal state to be adsorbed by the cartilage is not attained. If the food is

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[1] Dhar: J. Chem. Soc., 111, 694 (1917); J. Phys. Chem., 28, 943; (1924).

[2] Palit and Dhar: J. Phys. Chem., 29, 799 (1925); 30, 939 (1926).

[3] "Newer Knowledge of Nutrition," (1925).

[4] Z. anorg. Chem., 1927.

rich in phosphorus and lacks calcium there might be a tendency to form acid phosphate of calcium, which is soluble. Recent experimental researches of numerous workers show that even though the food is adequate in its calcium and phosphorus contents but lacks in vitamins A and D, rickets and osteomalacia and other bone troubles follow. We can explain these results from the following considerations:—

We have advanced the view that vitamins A and D act as activators or accelerators in the oxidation of fatty food materials in the animal body. In their absence the fat is not properly burnt and acidosis results, and consequently even in presence of $Ca^{\cdot\cdot}$ and PO_4''' ions, calcium phosphate cannot be formed in suitable concentration due to the presence of acids arising out of the incomplete combustion of food materials and hence rickets and other bone troubles will arise. This deficiency of vitamins can be partially compensated by light, because we have proved that the oxidation of fats by air is greatly accelerated by sunlight, and it is well known that light can prevent rickets to a certain extent. It will be interesting to note that Miss Hodgson[1] reported that, in her experience in many cases of rickets, acidosis developed at the height of the disease. Pritchard[2] stated his belief that the true cause of rickets is probably a relative excess of acid substances produced in the system. Burgess and Osman[3] reported three cases of acute rickets in which they found severe acidosis. It should be emphasised that iron preparations which we have proved to be able to accelerate the oxidation of fats should be very useful in rickets, and that is why milk should be used with the addition of a little iron preparation in the infant feeding.

It will be interesting to note that Tisdall and Harris[4] found the inorganic phosphorus content of normal serum from birth to twenty years to be remarkably constant at 5.6 milligrams per 100 c.c. of serum. At twenty years of age the phosphorus content drops sharply to 3.75 mgs and remains constant throughout adult life. During the period of union of fractures in adults they found that the phosphorus content of the serum should be raised to the level of about the same as that present in childhood.

Petersen[5] found it possible by dietic management to lower the phosphorus content of the blood of dogs to a point where the product of calcium times phosphorus was less than thirty. He concluded from his study that in the healing of fractures a definite relationship exists between the concentration of inorganic bone-forming elements in the serum and the rate of repair. If the phosphorus times the calcium product is again raised to their normal level, the fractured bones will unite. He applied these conclusions to the case of a man aged 47, who had a fractured bone and by improvement of diet and exposure to light he could easily join the fracture. These experi-

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[1] Lancet, 1921 II, 945.

[2] Brit. Med. J., 1923 I, 887.

[3] Lancet, 1924 I, 281.

[4] J. Am. Med. Assoc., 79, 884 (1922).

[5] Johns Hopkins Hosp. Bull., 35, 378 (1924).

mental results clearly follow from the consideration of the equilibrium:—
$3\ Ca'' + PO_4''' \rightleftarrows Ca_3(PO_4)_2$ (Colloidal)$\rightleftarrows Ca_3(PO_4)_3$(Solid in bones) already discussed.

We believe that the decrease in the amount of calcium phosphate existing in serum with increasing age is due toa gradual but a slow decrease of the alkalinity of the blood with age. In a foregoing paper we have shown that the concentration of the peptising agents present in the blood and serum increases with age because the percentage of water in the body decreases with age. Hence the amount of calcium phosphate which can remain in the colloidal condition would have increased because of the increase in the concentration of the peptising agents, but as a matter of fact, the concentration of calcium phosphate existing in the colloidal state in the serum decreases with age. This is because the metabolism and the amount of heat necessary for the body decreases with age and that the decreased metabolism may lead to a decrease in the alkalinity of the blood and a consequent decrease of calcium phosphate existing in the colloidal state in the blood and serum. In this connection it will be of interest to note that the requirement for vitamin A decreases with age. This is possibly because the requirement of the body heat becomes less with age and hence the presence of the accelerator of oxidations (vitamins) becomes less important with age. Moreover the rate of growth decreases with increasing age and hence the need of vitamin A decreases with age.

Summary and Conclusions

(1) Epidemic dropsy is not caused by fungus or poison in rice or mustard oil.

(2) Defective carbohydrate metabolism is the probable cause of beri-beri and epidemic dropsy.

(3) Light should prove useful in the treatment of metabolism and deficiency diseases like beri-beri, scurvy, pellagra, pernicious anaemia, epidemic dropsy, leukaemia, diabetes, gout, etc., because light can accelerate the oxidation of carbohydrates, fats and nitrogenous substances by air.

(4) Iron preparations should be efficacious in the treatment of deficiency and metabolism diseases, because in presence of iron preparations the oxidation of food materials by air is greatly increased.

(5) It seems likely that there is a definite equilibrium in the body controlling bone formation as represented by the following scheme:—
$3\ Ca^{\circ\circ} + 2\ PO_4''' \rightleftarrows Ca_3(PO_4)_2$ (Colloidal) $\rightleftarrows Ca_3(PO_4)_2$ (Solid in bones)
Decrease of alkalinity of the serum is the cause of defective bone formation.

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STABILITY OF THE SOLS OF TUNGSTIC, VANADIC AND SILICIC ACIDS UNDER DIFFERENT CONDITIONS

BY S. GHOSH AND N. R. DHAR

We[1] have shown that Odén's sulphur sol becomes unstable in presence of an alkali and stable in presence of an acid. These results seem at first sight to be abnormal because in most cases hydroxyl ion stabilises a negatively charged sol markedly and hydrogen ion exert a high coagulating effect on it. In one of our papers[2] on coagulation we have shown that OH′ ions possess remarkable stabilising influence on the sols of arsenious sulphide, antimony sulphide, gum dammar, mastic etc; whilst H˙ ions exert a sensitizing effect towards their coagulation by electrolytes. We have explained this peculiar behaviour of H˙ ions in stabilising and OH′ ions in sensitizing sulphur sol from the point of view that acids stabilise whilst alkalies decompose pentathionic acid, which is the stabilising electrolyte in Odén's sulphur sol.

It will be of interest to observe that silicic acid sol like Odén's sulphur sol becomes unstable in presence of small quantities of an alkali and stable by the addition of an acid. Many years ago Flemming[3] and Pappadà[4] observed that small concentrations of OH′ ions favour the gelation of silicic acid sol. Recently Freundlich and Cohn[5] observed that alkali possesses marked sensitizing influence on the coagulation of silicic acid sol by NaCl, $BaCl_2$, $CaCl_2$, etc. Similarly, it has been reported in several communications[6] in "Nature" that for silica and clay, the hydroxides of the metals of the alkalies and alkaline earths act as better coagulating agents than their corresponding chlorides. These results are analogous to those obtained with Odén's sulphur sol. Silicic acid sol is negatively charged and adsorbs large amounts of OH′ ions. It is, therefore, expected that OH′ ions should possess a stabilising influence on silicic acid sol, just as sols of $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, etc, are stabilised by an acid due to adsorption of H˙ ions by these positively charged hydroxide sols. In a previous communication[7] we have offered an explanation of this peculiar behaviour of silicic acid sol, and have concluded that similar behaviour towards H˙ and OH′ ions is expected from sols of tungstic acid, molybdic acid, vanadic acid, etc.

In this paper we shall present our results now obtained with silicic acid, tungstic acid, and vanadic acid sols from various points of view.

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[1] Kolloid-Z., 1928.

[2] Kolloid-Z., 39, 346 (1926).

[3] Z. physik. Chem., 41, 427 (1902).

[4] Gazz., 33, 272 (1903).

[5] Kolloid-Z., 39, 28 (1926).

[6] Compare Oakley and coworkers; Nature, Nov. 6, page 824, (1926); May 7, page 673, (1926). Also see Comber: J. Agr. Sci., 10, 425, (1920).

[7] loc. cit.

1. Tungstic Acid Sol

This sol was first prepared by Graham by adding an acid to sodium tungstate solution and then dialysing the mixture. This substance prepared by Graham's method contains a large proportion of tungstic acid in the form of true solution which passes out during the process of dialysis. The sol obtained by Graham's method is very stable towards electrolytes and is optically clear. We have, however, prepared tungstic acid sol in these investigations by first precipitating tungstic acid by an excess of HCl and then dialysing the precipitate in a parchment bag after washing the precipitate free from chloride. It has been observed that the white precipitate of tungstic acid obtained at low temperatures (8°C) is more easily converted into sol than the yellowish precipitate obtained at a higher temperature (30°C). The sol obtained by this method is almost optically clear at first, but gradually becomes turbid; and, finally, after two and a half months it becomes opaque with the precipitation of some tungstic acid. In order to test the validity of the Schulze-Hardy Law for this sol, coagulation experiments were carried on with different electrolytes, Table I.

TABLE I

Concentration of tungstic acid sol = 19.52 grms. NO_3 per litre.
2 c.c. of the sol is taken each time.
Total volume = 6 c.c. Time = 1 hour

Electrolyte		Amount to coagulate in c.c	Precipitation value
KOH	N/8.74	1.10 (turbid and partially dissolves)	0.022
KCl	N/4	0.90	0.038
NaCl	N/4	3.20	0.133
KNO_3	N/4	0.90	0.038
$BaCl_2$	N/80	1.30	0.003
$SrCl_2$	N/50	2.05	0.006
$Al(NO_3)_3$	N/50	1.15	0.004
HCl	0.665N	>4.0	—

It will be seen from Table I that the coagulating power of different electrolytes on this negatively charged sol is in the following decreasing order:

$BaCl_2 > Al(NO_3)_3 > SrCl_2 > KOH > KCl, KNO_3 > NaCl > HCl$.

Potassium hydroxide possesses greater coagulating power than sodium and potassium salts, which are, in their turn, better coagulating agents than hydrochloric acid. It is well known that hydrogen ions generally possess greater coagulating power than potassium or sodium ions for negatively charged sols. This remarkable behaviour of hydrogen ions towards tungstic acid sol suggests that the sol is stabilised by hydrogen ions. It is obvious that the greater precipitation value of $Al(NO_3)_3$ than that of $BaCl_2$ is due to the presence of $H^{\cdot}$ ions in $Al(NO_3)_3$ solution.

In Table II we shall record our results when tungstic acid sol is coagulated by different electrolytes at various dilutions of the sol:—

TABLE II

Sol A = 2 c.c. of tungstic acid sol containing 19.52 grs. of WO_3 per litre. Total volume = 6 c.c.; Time = 1 hour

Concentration of the sol.	Amount required to coagulate in c.c. KNO_3 N/4	$BaCl_2$ N/80	$Al(NO_3)_3$ N/50
2A	0.90	1.45	1.45
A	0.85	1.25	1.15
A/2	0.80	1.00	0.75

These results prove that tungstic acid sol behaves normally on dilution, i.e., the greater the concentration of the sol the greater is the amount of an electrolyte necessary for coagulation.

In previous papers[1] we have shown that a sol, which behaves normally towards dilution, also shows additive relationship when coagulated by mixtures of electrolytes of varying valency. In Table III the results are recorded when tungstic acid sol is coagulated with mixtures of KNO_3 and $BaCl_2$.

TABLE III

2 c.c. of the sol is taken each time. Volume = 6 c.c. Time = 1 hour

KNO_3 N/4 added in c.c.	$BaCl_2$ N/80 to coagulate in c.c. Observed	Calculated	Difference	% Difference
0	1.25	—	—	—
0.85	0	—	—	—
0.10	1.10	1.10	0	0
0.30	0.75	0.80	−0.05	6
0.50	0.45	0.51	−0.06	12.4

Table III proves that additive amounts of KNO_3 and $BaCl_2$ are necessary for the coagulation of this sol.

We have already shown that large amounts of HCl and small quantities of KOH are necessary to coagulate tungstic sol. The results recorded in Tables IV-V prove that $H^\cdot$ ions possess a stabilising influence whilst OH' ions possess a sensitizing influence on tungstic acid sol.

TABLE IV

Coagulation of tungstic acid sol by KCl in presence of HCl

2 c.c. of the sol is taken each time. Volume = 6 c.c. Time = 1 hour

HCl N/100 added in c.c.	KNO_3 N/4 to coagulate in c.c.
0	0.85
0.2	0.95
0.6	0.95
0.8	0.85

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[1] J. Phys. Chem., 29, 435, 659 (1925); 31, 187 (1927).

TABLE V

Coagulation of tungstic acid sol by KCl in presence of KOH

2 c.c. of the sol is taken each time. Volume = 6 c.c. Time = 1 hour

KOH N/8.74 added in c.c.	KNO_3 N/4 to coagulate in c.c.
0	0.85
0.1	0.75
0.2	0.65
0.5	0.30
1.0	<0.05
2.0	Could not be coagulated, as most of the colloid dissolves

In a previous paper[1] we have shown that OH′ ions possess a stabilising influence on sols of As_2S_3, Sb_2S_3 and mastic and that the sodium or potassium salt of a weak acid is required in larger quantities than the salt from a strong acid for coagulating the above negatively charged sols, because the sodium or potassium salt solution of the weak acids contain OH′ ions due to hydrolysis. In this paper we have studied the coagulation of tungstic acid sol by sodium salts of different weak acids and it is found that, unlike As_2S_3, Sb_2S_3 and mastic, these salts possess greater coagulating power than NaCl on tungstic acid sol. The experimental results are given in Table VI.

TABLE VI

2 c.c. of the sol is taken each time. Volume = 6 c.c. Time = 1 hour

Electrolyte	Amount to coagulate in c.c.	Precipitation value
NaCl N/2	1.35	0.113
CH_3COONa N/2	0.80	0.067
$NaNO_2$ N/2	0.95	0.079
C_6H_5COONa N/2	0.90	0.075
Na_2CO_3 N/2	0.75	0.063
HCl N/2	>4.0	—

Table VI shows that the coagulating power of different electrolytes are in the following decreasing order:—

$$Na_2CO_3 > CH_3COONa > C_6H_5COONa > NaNO_2 > NaCl > HCl,$$

sodium carbonate possessing the maximum coagulating influence. The dissociation constant of the different weak acids of which the sodium salts have been used, are in the following increasing order.

$$H_2CO_3 < CH_3COOH < C_6H_5COOH < HNO_2, \text{ and}$$

consequently sodium carbonate possesses largest amounts of OH′ ions.

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[1] Kolloid-Z., 39, 346 (1926).

In several communications[1] from these laboratories the effect of electrolytes on the viscosity of several sols has been investigated, and it has been observed that an increase in charge on the colloid particles leads to a decrease in its viscosity, whilst a decrease in charge makes the sol more viscous. In order to show that OH′ ions decrease and H˙ ions increase the charge on colloid particles of tungstic acid sol, we have investigated the effect of small quantities of alkali and acid on the viscosity of this sol. The results obtained are given in Table VII.

TABLE VII

Concentration of the sol = 19.52 grams. WO_3 per litre
Temperature = 30°C

	Viscosity
Water	0.00803
8 c.c. sol + 2 c.c. water	0.00869
8 c.c. sol + 1.8 c.c. water + 0.2 c.c N/100 HCl	0.00867
" + 1.5 c.c. water + 0.5 c.c. N/100 HCl	0.00866
" + 1.0 c.c. water + 1.0 c.c. N/100 HCl	0.00870
" + 1.8 c.c. water + 0.2 c.c. N/100 KOH	0.00871
" + 1.5 c.c. water + 0.5 c.c. N/100 KOH	0.00872
" + 1.0 c.c. water + 1.0 c.c. N/100 KOH	0.00868
" + 0.5 c.c. water + 1.5 c.c. N/100 KOH	0.00863

A perusal of Table VII shows that the viscosity of tungstic acid sol is at first slightly increased by KOH, but is decreased on further addition of alkali. On the other hand, the viscosity first decreases and then decreases on adding increasing amounts of HCl. These results, therefore, prove that alkali causes a decrease in the electric charge on the colloid particles. The subsequent decrease in the viscosity is necessarily due to the fact that some colloidal tungstic acid is dissolved by increasing amounts of alkali. HCl, however, first increases the electric charge on the colloid particles, and finally, as the concentration of H˙ ions is increased, they exert a coagulating effect, and this results in an increase in the viscosity of the sol.

We have observed that tungstic acid sol becomes turbid on keeping for a long time. Wassiljewa[1] has shown that a fresh sample of tungstic acid sol is easily reduced by formaldehyde, grape sugar, and other reducing agents in presence of light to a blue-coloured lower oxide. On ageing, tungstic acid sol partly loses its photochemical activity and cannot be reduced so readily on exposure to light. If, however, the sol is boiled it regains its photosensitivity. The results obtained on the stability, conductivity and viscosity of tungstic acid sol on ageing and boiling are recorded in Tables VIII-XI.

Our experimental results given in Tables VIII and IX show that the sol of tungstic acid becomes more viscous, less conducting, and more unstable on ageing. Tables X and XI show that the sol beomes unstable on boiling, but

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[1] Z. Elektrochemie, 31, 261 (1925); J. Phys. Chem., 29, 1556 (1925); 30, 1646 (1926); Z. anorg. allgem. Chem., 152, 393 (1926); Kolloid-Z., 42, 124 (1927).

TABLE VIII

Influence of ageing on the viscosity and specific conductivity of tungstic acid sol.
Concentration of the sol = 19.52 grms. WO_3 per litre
Temperature = 30°C

Date	Specific conductivity	Viscosity (8 cc. sol + 2 c.c. water)
32. Oct. '27	4.12×10^{-3}	0.008309
31. Oct. '27	3.883×10^{-3}	0.008411
2. Nov. '27	3.769×10^{-3}	—
4. Nov. '27	3.728×10^{-3}	0.008710
18. Nov. '27	3.632×10^{-3}	0.008795

(A portion has coagulated)

TABLE IX

Influence of ageing on the coagulation of tungstic acid sol
Concentration of the sol = 19.52 grms. WO_3 per litre.
Amount of sol taken each time = 2 c.c.
Volume = 6 c.c. Time = 1 hour

Date	Amount of electrolyte to coagulate in c.c.	
	KNO_3 N/4	$BaCl_2$ N/80
23. Oct. '27	0.90	1.30
31. Oct. '27	0.80	1.20

TABLE X

Influence of boiling on the viscosity, specific conductivity
and hydrogen ion concentration of tungstic acid sol.

Sol	Specific conductivity	pH value	Viscosity
Unboiled	4.129×10^{-3}	3.0	0.008309
Boiled	4.298×10^{-3}	2.9	0.008213

TABLE XI

Influence of boiling on the coagulation of tungstic acid sol
Amount of sol taken each time = 1 c.c.
Volume = 6 c.c. Time = 1 hour

Sol	Amount of electrolyte to coagulate in c.c.	
	KNO_3 N/4	$BaCl_2$ N/80
Unboiled	0.7	1.0
Boiled	0.6	0.9

the viscosity of the sol decreases and the specific conductivity increases because of the increase in the hydrogen ion concentration of the sol on boiling. These results are interesting and will be discussed later on.

The influence of acid and alkali on the electrical conductivity of tungstic acid sol has also been investigated and the results are reproduced in Table XII.

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[1] Z. wiss. Phot., 12, 1 (1913).

TABLE XII

Concentration of the sol = 19.52 grms WO_3 per litre
Temperature = 30°C

Solution	Sp. conductivity (observed)	Sp. conductivity of the mixture (calculated)
6 c.c. sol + 2 c.c. water	$2.723 \times 10^{+3}$	—
" + 2 c.c. KOH N/100	2.576×10^{-3}	3.608×10^{-3}
6 c.c. water + "	1.032×10^{-3}	—
6 c.c. water + 2 c.c. HCl N/100	1.482×10^{-3}	—
6 c.c. sol + 2 c.c. HCl N/100	3.518×10^{-3}	4.205×10^{-3}

Table XI proves that both KOH and HCl depress the conductivity of tungstic acid sol.

2. Vanadium Pentoxide Sol

This sol is prepared by precipitating V_2O_5 from ammonium vanadate by HCl, and then on washing the precipitate almost free from HCl, it passes into colloidal solution. This is now dialysed for a week to free it from electrolytes. In this paper we have investigated the influence of alkali and acid on its coagulation by electrolytes and the results are given in Tables XIII-XIV.

TABLE XIII

Coagulation of vanadium pentoxide sol by KCl in presence of NH_4OH.
Concentration of the sol = 7.44 grms V_2O_5 per litre
2 c.c. of the sol is taken each time.
Volume = 6 c.c. Time = 15 minutes

NH_4OH N/10 added in c.c.	KCl N/20 to coagulate in c.c.	NH_4OH N/10 added in c.c.	KCl N/20 to coagulate in c.c.
0	1.55	0.5	1.10
0.2	1.50	0.8	0.75

TABLE XIV

Coagulation of vanadium pentoxide sol by KCl in presence of HCl

HCl N/100 added in c.c.	KCl N/20 to coagulate in c.c.	HCl N/100 added in c.c.	KCl N/20 to coagulate in c.c.
0	1.55	0.10	1.55
0.05	1.60	0.20	1.55

Our results in Tables XIII and XIV definitely prove that a decrease in H' ion concentration by an alkali makes the sol unstable, whilst an increase in H' ion concentration first increases and then slightly decreases the stability of vanadium pentoxide sol.

We have also carried on experiments on the viscosity of this sol in presence of small amounts of alkali and acid. The preliminary results in Table XIV were obtained with an old sample of vanadium pentoxide sol in presence of KOH.

TABLE XV

Concentration of the sol = 7.72 grms V_2O_5 per litre. Temperature = 30°c.

	Viscosity
Water	0.00803
9.5 c.c. sol + 0.4 c.c. water + 0.1 c.c. N/100 KOH	0.02131
9.5 c.c sol + 0.1 c.c water + 0.4 c.c. N/100 KOH	0.02015
9.5 c.c. sol + 0.5 c.c. water	0.02071

These results show that there is a distinct increase in the viscosity of vanadium pentoxide sol by 0.1 c.c. N/100 KOH, whilst the viscosity diminishes in presence of 0.4 c.c. N/100 KOH.

In Table XVI we shall record our results obtained from a newly prepared sol both in the presence of an acid and an alkali.

TABLE XVI

Concentration of the sol = 7.44 grms V_2O_5 per litre. Temp. = 30°c.

	Viscosity
Water	0.00803
9 c.c. sol + 1 c.c. water	0.01136
9 c.c. sol + 0.95 c.c. water + 0.05 c.c. N/100 HCl	0.01132
9 c.c. sol + 0.9 c.c. water + 0.1 c.c. N/100 HCl	0.01128
9 c.c. sol + 0.85 c.c. water + 0.15 c.c. N/100 HCl	0.01127
9 c.c. sol + 0.75 c.c. water + 0.25 c.c. N/100 HCl	0.01119
9 c.c. sol + 0.5 c.c. water + 0.5 c.c. N/100 HCl	0.01132
9 c.c. sol + — + 1.0 c.c. N/100	0.01142
9 c.c. sol + 0.95 c.c. water + 0.05 c.c. N/100 NH_4OH	0.01141
9 c.c. sol + 0.9 c.c. water + 0.1 cc. N/100 NH_4OH	0.01135

The above table conclusively proves that a drop of NH_4OH causes first an increase in the viscosity of vanadium pentoxide and then the viscosity decreases when more of NH_4OH is used. On the other hand, the viscosity of V_2O_5 sol first decreases and then increases in the presence of increasing amounts of HCl. These results are similar to those obtained with tungstic acid sol in presence of varying hydrogen ion concentration.

We shall now present our results obtained on the coagulation of vanadium pentoxide sol by different hydrolysable salts, Table XVII.

The coagulating powers of different electrolytes are in the following decreasing order:—

$$CH_3COONa > C_6H_5\,COONa > NaNO_3 > NaCl > HCl$$

It is evident from the above series that the electrolyte containing the least amount of hydrogen ions is the best coagulating agent. This is as we have already shown, is due to the fact that OH′ ions possess a sensitizing influence and H ions a stabilising effect.

We have investigated the influence of ageing on the stability of vanadium pentoxide sol and the results obtained given in Table XVIII.

TABLE XVII

Concentration of the sol = 7.44 grms V_2O_5 per litre
Amount of sol taken each time = 2 c.c. Volume = 6 c.c.
Time = 15 minutes

Electrolyte		Amount to coagulate in c.c.	Precipitation value
NaCl	N/20	1.65	0.0137
CH_3COONa	N/20	1.05	0.0088
$NaNO_2$	N/20	1.20	0.0100
C_6H_5COONa	N/20	1.15	0.0096
HCl	N/2	0.60	0.0500

TABLE XVIII

Concentration of the sol = 7.44 grms V_2O_5 per litre. 2 c.c. of the sol is taken each time.
Volume = 6 c.c. Time = 15 minutes

Date	Electrolyte to coagulate in c.c.	
	NaCl N/20	$BaCl_2$/500
10. Nov. '27	1.65	1.30
29. Nov. '27	1.45	1.15

TABLE XIX[1]

Change of viscosity of vanadium pentoxide sol with time
Concentration of the sol = 1.093 grm V_2O_5 per litre.

Date	Viscosity (compared with water)	Date	Viscosity (compared with water)
30. Nov. '22	1.045	4. Dec. '22	1.080
6. Dec. '22	1.085	8. Dec. '22	1.100
12. Dec. '22	1.095	18. Dec. '22	1.110
28. Dec. '22	1.132	17. Jan. '23	1.180
7. Feb. '23	1.210	17. April '23	1.300

TABLE XX[2]

Change of electrical conductivity of vanadium pentoxide sol with time
Concentration of the sol = 1.020 grm V_2O_5 per litre.

Date	Specific conductivity
10. April '22	6.300×10^{-4}
9. May '22	5.140×10^{-4}
22. June '22	4.765×10^{-4}
9. Sept. '22	4.66×10^{-4}
16. Jan. '23	4.19×10^{-4}

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[1] Z. anorg. allgem. Chem., **152**, 399 (1926).

[2] Compare Gessner: Kolloidchem. Beihefte, **19**, 283 (1924).

The results prove that vanadium pentoxide sol becomes unstable on keeping. We have already shown that a dialysed sol of vanadium pentoxide when kept becomes unstable and sets to a jelly. Moreover a colloidal solution of vanadium pentoxide becomes more viscous and less conducting on ageing as shown in Tables XIX-XX.

We have found that vanadium pentoxide sol also becomes unstable on boiling and its electrical conductivity markedly increases. The results are given in Table XXI.

TABLE XXI

2 c.c. of the sol containing 7.44 grams of V_2O_5 is taken each time
Volume = 6 c.c. Time = 15 minutes

Sol	Amount of electrolyte to coagulate in c.c.	
	KNO_3 N/20	$BaCl_2$ N/500
Boiled	1.30	1.70
Unboiled	1.45	1.85

	Specific Conductivity
Boiled	1.203×10^{-3}
Unboiled	1.075×10^{-3}

3. Silicic Acid Sol

In a recent paper Freundlich and Cohn[1] have studied carefully the coagulation or gelation of this sol by KCl, NaCl, $CaCl_2$, and $BaCl_2$ in presence of varying amounts of NH_4OH and have observed that the sol becomes unstable by the addition of NH_4OH. When, however, larger concentrations of NH_4OH are used, the sol is no more gelatinised by any of the above electrolytes, and the conductivity of the solution is highly increased. We have investigated the influence of alkali and acid on the viscosity of silicic acid[2] sol, Tables XXII-XXIII.

TABLE XXII

Change of viscosity of a concentrated sol of silicic acid in presence of an alkali.
Concentration of the sol = 22.54 grms SiO_2 per litre
Temperature = 30°C

Water	Viscosity
	0.00803
8 c.c. sol + 4 c.c. water	0.01111
8 c.c. sol + 4 c.c. N/100 KOH	0.01451

Tables XXII-XXIII prove that silicic acid sol first becomes more viscous in presence of KOH. When larger amounts of the alkali are used the viscosity decreases. On the other hand, the viscosity first decreases and then increases with the increasing amounts of the acid.

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[1] loc. cit.

[2] Silicic acid sol is prepared by adding $SiCl_4$ in small quantities to cold water and then dialyzing till it is free from HCl.

TABLE XXIII

Change of viscosity of a dilute sol of silicic acid in presence of an alkali and in acid

Concentration of the sol = 8.66 grms SiO_2 per litre. Temperature = 30°

	Viscosity
9 c.c. sol + 1 c.c. water	0.00922
" + 1 c.c. N/1000 KOH	0.00923
" + 1 c.c. N/100 KOH	0.00936
" + 1 c.c. N/50 KOH	0.00927
" + 1 c.c. N/10 KOH	0.00918
" + 1 c.c. N/500 HCl	0.00902
" + 1 c.c. N/20 HCl	0.00924
" + 1 c.c. N/2 HCl	0.00926

We shall now reproduce some of our results obtained in a previous paper[1] on the change of viscosity and electrical conductivity of silicic acid sol on ageing, Table XXIV.

TABLE XXIV

Concentration of the sol = 12.075 grms SiO_2 per litre
Temperature = 30°C.

Date	Viscosity	Specific Conductivity
6. April '27	0.00851	2.045×10^{-3}
7. April '27	0.00872	2.11×10^{-3}
2. May '27	0.00919	2.14×10^{-3}
13. July '27	0.01121	2.10×10^{-3}

From these results we find that the viscosity of the sol prepared in the cold continuously increases with time. The specific conductivity of the sol first increases and then decreases after a limiting value.

A silicic acid sol was also prepared in the hot condition and the influence of ageing on the viscosity and specific conductivity of this sol has been investigated.

The results are given in Table XXV.

TABLE XXV

Concentration of the sol = 6.17 grs. SiO_2 per litre
Temperature = 30°

Date	Viscosity	Specific Conductivity
4. April '27	0.01007	5.75×10^{-6}
2. May '27	0.01021	6.1×10^{-5}
3. July '27	0.06123	—

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[1] Z. anorg. allgem. Chem., **168**, 209 (1927).

In this case also, the viscosity of the sol prepared in the hot condition increases with time and the specific conductivity also increases on ageing. It is of interest to note that the sol prepared in the hot condition becomes more viscous on ageing then the sol prepared in the cold. This is because the sol prepared in the hot condition is more unstable than the sol prepared in the cold.

Discussion

Our experimental results on the coagulation of tungstic acid and vanadium pentoxide sols show that these sols become unstable in presence of an alkali and stable in the presence of an acid. Similar results have been obtained with SiO_2 sol by other investigators. We have also observed that for tungstic acid and vanadium pentoxide sols the viscosity increases markedly and the electrical conductivity of the sols diminishes on ageing. Our results show that the viscosity and specific conductivity of silicic acid sol increase continuously with time. We are of the opinion that all these facts observed with the sols of tungstic acid, vanadic acid and silicic acid can be explained on the view that all these sols contain a part of these acids in the molecular condition, and that the dissolved part gradually polymerises and finally passes into the colloidal state with time. On the other hand, colloid particles also aggregate to form bigger particles and thus the sols become unstable on keeping.

TABLE XXVI

Concentration of the sol = 7.44 grs. V_2O_5 per litre

Sol	Amount of V_2O_5 dissolved per 10 c.c. of the sol in grm.
Unboiled sol on 10. Nov. '27	0.0038
Unboiled sol on 12. Dec. '27	0.0033
Boiled sol	0.0072
10 c.c. Unboiled sol + 0.5 c.c. N/100 NH_4OH	0.0121

The high electrical conductivity of tungstic acid sol and its distinct acidity (pH value 3.0) proves that fairly large amounts of tungstic acid are present in the dissolved condition. We have also observed that after coagulating a sol of tungstic acid by KNO_3, the filtrate, which is perfectly clear and does not contain any colloid, gives a white precipitate of silver tungstate with $AgNO_3$. Similarly, vanadium pentoxide sol also gives a yellowish filtrate of dissolved vanadic acid after coagulating with an electrolyte. We have estimated this dissolved vanadic acid in a freshly prepared as well as in an aged sol of vanadium pentoxide. The sol was coagulated by KNO_3 and vanadic acid in solution is filtered which was then reduced by a current of sulphur dioxide. The excess of sulphur dioxide was boiled off and the reduced vanadic acid is titrated with a standard permanganate. The amounts of dissolved vanadic acid in a boiled sol of V_2O_5 and in a sol containing a few drops of NH_4OH are also determined and the results are given in Table XXVI.

The above results show that in a sol of V_2O_5 5.1% vanadic acid is present in solution and this amount decreases to 4.4% after 32 days. On the other hand, the amounts of V_2O_5 in solution increase by either heating the sol or by adding a few drops of ammonia, the amount of dissolved vanadic acid in the boiled sol is 9.7% and in presence of 0.5 c.c. N/150 NH_4OH, it is 16.3%.

Mylius and Groschuff,[1] working with silicic acid sol, came to the same conclusion. They believe that at the moment of formation of silicic acid from water glass, it exists in the molecular solution, which passes unchanged through a parchment dialyser. Colloidal particles then result from polymerisation of the simple silicic acid molecules on keeping the solution and this is shown by the increase of molecular weight for many weeks. Several workers[2] have concluded that this ageing process leads to the formation of highly polymerised colloid particles and finally to crystalline silica.

Several years ago Wassiljewa[3] has shown that freshly prepared tungstic acid is easily reduced to a blue lower oxide of tungsten by different reducing agents when exposed to light. The sol, however, becomes less photochemically active with time and cannot be easily reduced in presence of light. We believe that this is due to the fact that most of the tungstic acid present in the molecular condition polymerises to larger molecules or to colloid particles, which are not as chemically active as the simple molecules.

We are of the opinion that increase in the viscosity of the sols of tungstic acid, vanadic acid and silicic acid with time originates from the aggregation of the dissolved substances to form more of colloidal particles. This decrease of the substances present in the dissolved condition with time is also confirmed by the fact that the electrical conductivity of tungstic and vanadic acid sols decreases on ageing. The decrease in the specific conductivity of these sols on ageing is more marked than that which can be attributed to the increase in viscosity with time. The electrical conductivity of silicic acid sol, however, increases on ageing. This is most probably due to the fact that all colloidal particles have a tendency to give out the adsorbed electrolyte on keeping. Thus we have shown[4] that sols of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc, become more conducting with time because they give out the adsorbed electrolyte on ageing. Consequently silicic acid sol which possesses an electrical conductivity mostly due to the free electrolyte in the sol shows an increase in the electrical conductivity as more of adsorbed electrolyte is given out on ageing. The depression of the electrical conductivity due to the polymerisation of silicic acid molecules is more than counterbalanced by the giving out of the adsorbed electrolyte in larger quantities with time. It is well known that silicic acid is a very weak acid, and therefore, its electrical conductivity is necessarily very small. On the other hand, the depression of the electrical conductivity of vanadic and tungstic acids on keeping due to the polymerisation of the dissolved acids is more prominent than the tendency of an increase in the electrical conductivity due to the liberation of adsorbed

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[1] Ber., 39, 116 (1906); also see Norton and Roth: J. Am. Chem. Soc., 19, 832 (1897).

[2] Cf. Schwarz and coworkers: Kolloidchem. Beihefte 19, 171 (1924); Kolloid-Z., 28, 77 (1921); Grundmann: Kolloidchem. Beihefte, 18, 197 (1923).

[3] Loc. cit.

[4] Z. anorg. allgem. Chem., 162, 237; 168, 209 (1927); Kolloid-Z., 42, 20 (1927).

electrolyte on ageing. The sols of tungstic, vanadic and silicic acids all become unstable towards their coagulation by electrolytes on keeping, and this is obviously due to the fact that the colloid particles also aggregate to form bigger particles, and consequently lose their stability.

The stabilising influence of traces of an acid, and the sensitizing effect of small concentration of an alkali for the sols of silicic, tungstic and vanadic acids in explainable from the following points of view:—

We have already shown that a portion of these substances is present in the molecular condition. Some of this is in equlibrium with the complex acids originating from the association of the simple molecular compounds.

Now, if an alkali is added to a silicic acid sol it will react on the unpolymerised acid molecules readily because of its greater chemical reactivity than that of the polymerised molecules. Hence the amount of polymerised molecules will decrease and more of unpolymerised molecules will be formed in order to restore the equilibrium. The polymerised molecules of the acid gives out a complex negative ion, which is adsorbed more by silicic acid sol than a simple ion. We have shown[1] that the amount of adsorption is greater for a complex and heavy ion than a simple one. On the addition of an alkali, the concentration of the complex ion decreases and hence its amount of adsorption by silicic sol also decreases. Thus the electrical charge and stability of the sol becomes less in presence of small quantities of alkali.

On the other hand, presence of $H^\cdot$ ions increases the complexity of the anions so that more of anions are now adsorbed by the sol which becomes necessarily stabilised. In a recent paper Schulz and Jander[2] have shown that tungstate ion becomes more complex in nature in presence of $H^\cdot$ ions and simple by the introduction of OH' ions. Our results with vanadium pentoxide sol also show that more of vanadic acid comes in true solution when a little alkali is added to the sol of V_2O_5.

In this paper we have investigated the viscosity of these sols in presence of traces of alkali and acid, and we have observed that in all cases, that the first addition causes an increase in the viscosity of the sol, whilst acids when added in small amounts, decrease the viscosity of the sol. In several communications it has been proved that an increase in the viscosity of a sol originates from a decrease in the electric charge on the colloid particles, whereas an increase in the electric charge of colloid particles makes the sol less viscous. Consequently, our results on the viscosity of these sols in presence of varying amounts of $H^\cdot$ and OH' ions accord a conclusive evidence that the electric charge of colloid particles decreases by the introduction of OH' ions and $H^\cdot$ ions increase their electrical charge. When, however, larger amounts of an alkali are used the viscosity naturally falls because some of the colloidal substance now passes into true solution. On the other hand, the viscosity of the sols increases on adding larger quantities of HCl as the aggregation may increase to such an extent as to form more colloidal particles

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[1] Kolloid-Z., 34, 144 (1924).

[2] Z. anorg. allgem. Chem., 26, 141 (1927).

and then H˙ ions in their turn may exert a coagulating effect. It may be of interest to point out here that when larger amounts of an alkali are used the sol may become stable because of the formation of large amounts of the dissolved salts formed by the interaction of the alkali and the colloid itself. These salts will give out anions in abundance which can be adsorbed by the colloid particles and thus the sol will be stabilized. Similarly, larger quantities of an acid favour the coagulation of the sols, because H˙ ions exert a coagulating effect at higher concentrations. Several investigators have observed with SiO_2 sol that its gelation is favoured or checked by a certain optimum concentration of OH′ or H˙ ions respectively, beyond which OH′ ions do not exert a coagulating effect whilst H. ions help the gelation of SiO_2 sol.

This influence of H˙ ions on the gelation of silicic acid sol has been noted long ago and it may be of interest to consider here some of the views of other workers on the peculiar behaviour of SiO_2 sol. Bancroft[1] attributes the increase in the speed of gelation by the addition of OH′ ions to the greater adsorption of cations in presence of an alkali. Thus Mattson[2] has shown that very large amounts of Ca˙˙ and Ba˙˙ ions are adsorbed by kaolin or quartz in presence of NaOH. It should be pointed out here that an addition of H˙ ions to the precipitates of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc, increases markedly the adsorption of anions by these hydroxides, but it is well known that H˙ ions stabilise these sols towards their coagulation by anions.

On the other hand, Freundlich and Cohn believe that alkali changes the degree of hydration of silicic acid, and thus changes the lyophilic SiO_2 to a lyophobe, and these sols are believed to be more sensitive to electrolytes. We are of the opinion that this view of Freundlich and Cohn cannot find support from our measurements of viscosity of this sol with varying amounts of OH′ and H˙ ions, where we have observed a distinct increase in the viscosity of the sols on addition of an alkali. It is obvious that an increase in viscosity is associated with an increase in the degree of hydration of the colloid particles and therefore, it is more lyophilic in nature in presence of an alkali and this is the opposite of what Freundlich and Cohn have assumed. On the other hand, we are of the opinion that this increase in viscosity originates from the decrease in the charge on the colloid particles in presence of an alkali. In a recent paper Pauli and Valko[3] have shown that the cataphoretic movement of colloidal SiO_2 is far less in presence of salts of weak acids than in presence of KCl. In Table XXVII some of their results are reproduced.

The above results of Pauli and Valko prove conclusively that the silicic acid sol moved more slowly in presence of CH_3COOK, $NaHCO_3$ and sodium p-oxybenzoate than in presence of KCl, and consequently the colloid particles appear less charged in the presence of OH′ ions obtained from the hy-

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[1] "Applied Colloid Chemistry," 137, 296 (1926).

[2] Kolloidchem. Beihefte, 14, 227 (1922).

[3] Kolloid-Z., 38, 289 (1926).

drolysis of the salts of the weak acids. Moreover we have shown in this paper that sols of tungstic acid and V_2O_5 require smaller quantities of hydrolysable salts and larger quantities of HCl than NaCl for their coagulation.

We have observed that sols of tungstic acid and vanadic acid become more unstable towards their coagulation, become more conducting and less viscous when heated. We are of the opinion that this occurs because at higher temperatures the complex acids existing in solution decompose to form simpler, molecules and as the complexity of the ion which is adsorbed by the sol, decreases, the amount, of adsorption of the stabilising ion also decreases and thus the sol becomes unstable on boiling. Moreover the electric conductivity of the sol is increased on heating because the simple and more conducting molecules increase in the solution. Side by side with this we should also take into account increased ageing of the colloid particles on boiling, and thus the loss of the adsorbed electrolyte is accentuated on boiling and makes the sol unstable. It is well known that by boiling colloids lose their adsorbed water and thus become less hydrated and less viscous. We have observed that a sol of silicic acid containing 22.54 grms. SiO_2 per litre sets to a stiff jelly on heating. Pauli and Valko have observed that a boiled sol of silicic acid becomes unstable towards electrolytes. Similarly, Flemming has shown that the time required for gelation of a concentrated silica sol is halved when the temperature is raised from 18° to 25°.

TABLE XXVII

Sol Number	Electrolyte	Velocity 10^4 c.m. per second
X	KCl	49.7
X	CH_3 CooK	25.7
XV	KCl	54.8
XV	CH_3CooK	30.3
XV	Na-p-oxybenzoate	29.1
XIX	KCl	24.2
XIX	$NaHCO_3$	20.8

Kruyt and Postma[1] have also determined the change of viscosity of silicic acid sol with time. They observed that the sol, which does not contain any free sodium silicate shows an increase in viscosity on ageing and also by adding an alkali, whilst the addition HCl causes at first a decrease in the viscosity. Kruyt and Postma have explained this change of viscosity on the view that an increased viscosity results from an increase in the electrical charge on the colloid particles due to addition of an alkali and decrease in viscosity from a decrease in the electric charge by the presence of an acid. This view seems to be incorrect as it has been repeatedly observed with more than twenty sols and it has been proved mathematically that the increase in the electric charge on the colloid particles always results with a decrease

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[1] Rev. Trav. chim., 44, 765 (1925).

in viscosity of the sols and vice-versa. Moreover, it is well known that silicic acid sol becomes unstable on the addition of an alkali and gelation is more rapid by electrolytes in its presence. We are, therefore, led to conclude that the increase in viscosity by the addition of alkali is due to the decrease in the electric charge of colloid particles.

Grundmann[1] has shown that with time the charge on silicic acid sol becomes more negative in presence of an acid and it reaches a maximum and then it falls and finally becomes positive. Moreover, the electric conductivity of a mixture of silicic acid sol and HCl falls off with time. These results can be explained from the point of view that the sol becomes stable and the charge increases in presence of small quantities of an acid as has already been explained. The decrease in the electrical charge of a sol in presence of HCl and its becoming positively charged with time, and a decrease in the electrical conductivity with time, are caused by the actual chemical reaction of HCl on silicic acid sol.

Summary and Conclusion

(1) Tungstic acid has been found to follow the Schulze-Hardy law. Concentrated sol requires more of an electrolyte to coagulate it than a dilute one and additive amounts of KNO_3 and $BaCl_2$ are required to coagulate the sol when it is precipitated by their mixtures.

(2) Sols of tungstic and vanadic acids require more of an acid and lesser amounts of the salts of weak acids to coagulate them than NaCl, KNO_3, etc.

(3) It has been shown that like silicic acid sol, the colloidal tungstic and vanadic acids are stabilised by an acid and sensitized by an alkali towards their coagulation by an electrolyte.

(4) The viscosities of the sols of silicic, tungstic, and vanadic acids increase in presence of traces of an alkali and decrease with small amounts of an acid.

(5) It has been observed that these sols contain some molecules in true solution and these dissolved molecules polymerise to form complex molecules by an increase in $H^\cdot$ ion concentration. On the other hand, the complex molecules become more simple in presence of OH' ions; and consequently the colloid particles adsorb more of stabilising anions in presence of an acid than in presence of an alkali.

(6) Viscosity and specific conductivity of the sols of tungstic and vanadic acids have been found to increase and decrease respectively with time. Silicic acid sol also becomes more viscous but more conducting on ageing.

(7) Boiling makes the sols of silicic, vanadic, and tungstic acids unstable.

It has been found that the sols of tungstic and vanadic acids become more conducting and less viscous on boiling.

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February 25, 1928.

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[1] Kolloidchem. Beihefte, 18, 197 (1923).

THE VAPOR PRESSURE OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA*

BY WARREN C. JOHNSON AND ALBERT W. MEYER

It is essential that the vapor pressures of solutions of the alkali metals in liquid ammonia be known so that the true concentration of any solution may be readily determined in the various investigations of its physical properties. These vapor pressure measurements are required at several temperatures and over a considerable range of concentration. Data are available for solutions of sodium[1] dissolved in liquid ammonia at many different temperatures, and for solutions of lithium[2] at −39.4°. Joannis has measured the vapor pressures of saturated solutions of potassium in liquid ammonia at temperatures ranging from −20° to +40°, and, in addition, has determined a few values of the vapor pressure of concentrated solutions of this metal at 0° and at 8.44°.

The pressure-composition curve offers a means of determining the solubility of the alkali metal in liquid ammonia at any given temperature. When ammonia is added to the metal, the resulting solution shows a constant vapor pressure, that of the saturated solution, as long as any undissolved metal remains. The change in the vapor pressure in passing from the saturated solution to those less concentrated in metal is very abrupt. It is possible to obtain several points on the curve in this region by careful manipulation in the experimental procedure. When this curve is extrapolated to intersect the horizontal line representing the vapor pressure of the saturated solution, there is obtained a point corresponding to the composition of the saturated solution. By this procedure, Joannis has found that, at 0° and 8.44°, 1 gram atom of potassium dissolves in 4.31 and 4.37 gram molecules of ammonia respectively. According to these values the solubility of potassium decreases as the temperature is increased from 0° to 8.44°. Since he records only two values at 0° at concentrations less than saturation, it is quite probable that the extrapolation he made to determine the solubility is considerably in error.

Ruff and Geisel[3] have determined the solubility of potassium in liquid ammonia by an entirely independent method. An amount of ammonia, insufficient to dissolve all the metal, was added to metallic potassium in small tubes. Above the mixtures was placed some cotton wadding and the upper end of the tubes was sealed. The tubes containing the material were then agitated for three hours to insure saturation. After this period they were

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* Contribution from the Kent Chemical Laboratory of the University of Chicago.

[1] Joannis: Ann. Chim., (8) 7, 5 (1906); Kraus, Carney and Johnson: J. Am. Chem. Soc., 49, 2206 (1927).

[2] Kraus and Johnson: J. Am. Chem. Soc., 47, 725 (1925).

[3] Ruff and Geisel: Ber., 39, 831 (1906).

inverted to allow the solution to filter through the wadding. When an amount sufficient for analysis had filtered, the tubes were immediately placed in a Dewar flask containing liquid air, in order to freeze the entire contents. Then the bottom part of each tube was broken off immediately above the saturated solution without allowing the contents to melt. The solution was finally analyzed according to the usual procedures. These investigators used this method to prepare and analyze saturated solutions of potassium in liquid ammonia. At 0°, −50° and −100° the composition of the saturated solutions was found to be 4.74, 4.79 and 4.82 gram molecules of ammonia respectively per gram atom of potassium. According to these values the solubility of potassium in liquid ammonia increases slightly with increasing temperature over the range from −100° to 0°.

Kraus and Lucasse[1] were able to determine the composition of a saturated solution of potassium in liquid ammonia by measuring the specific conductance as a function of the concentration. They found that at −33.5° one gram atom of potassium is dissolved in 4.87 gram molecules of ammonia.

The present investigation was undertaken to determine the vapor pressures of solution of potassium dissolved in liquid ammonia at various concentrations at the temperatures, 0°, −33.5° and −50.38°. The solubility of potassium in ammonia is obtained from the data.

Experimental Part

The apparatus was so designed that the vapor pressures could be readily determined for a series of concentrations ranging from that of a saturated solution to one quite dilute in dissolved metal. The method employed was essentially the same as that used by Kraus and Johnson in their measurements with lithium solutions. A soda-glass tube approximately 30 mm. in diameter, having a total capacity of about 150 cc., served as a container for the solutions. A glass stirrer supported by a Chromel wire spring, which was hung inside the tube, was used to agitate the solutions in order to facilitate the establishment of equilibrium conditions. The stirrer contained a cylindrical iron core which was actuated by passing an intermittent current through an external solenoid. The pressure was measured by means of a mercury manometer back of which was placed coordinate paper graduated in millimeters and mounted on a steel plate.

The ammonia introduced was measured in pipet cells graduated in 0.01 cc. and the manipulation was carried out according to the method of Kraus.[2] The volumes of the entire pipet system, of the lines leading to the manometers, and of the connecting tubes were determined by allowing ammonia gas to expand from a known volume and pressure into these various parts of the apparatus, the pressure being observed after each successive expansion. Fairly accurate values of these volumes were necessary in order that corrections might be applied for the amount of ammonia present in the vapor

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[1] Kraus and Lucasse: J. Am. Chem. Soc., 43, 2529 (1921).

[2] Kraus: J. Am. Chem. Soc., 43, 749 (1921).

state after each introduction of liquid ammonia from the pipet cells, and for the amount of vapor between the solution and the manometer after equilibrium has been established.

The metallic potassium was introduced into the tube through a fine capillary according to the method of Kraus and Lucasse.[1] As soon as the capillary was sealed off, the vapor-pressure tube and the pipet lines were exhausted by means of a mercury vapor pump supported by a Hy-Vac oil pump. A measured amount of ammonia was then introduced from a pipet cell and solution of the metal was accelerated by putting the stirrer into operation. After the solution had been agitated for several minutes and the vapor pressure appeared to be constant, the manometer reading was noted, a small amount of ammonia vapor was withdrawn, and the pressure was again observed. In this manner equilibrium was approached from both sides and the procedure served as a means for determining true equilibrium pressures.

In order to withdraw ammonia, the vapor-pressure tube was connected to a larger tube having a capacity of 550 cc. which in turn was connected to a second manometer. When an amount of ammonia more than sufficient for saturation had been added to the potassium, the vapor above the solution was allowed to expand into the large reservoir, the pressure was observed on the second manometer and the solution was allowed to come to equilibrium again. The ammonia gas was then pumped out of the reservoir, the vapor pressure of the solution was noted, and the above process for withdrawing additional ammonia was repeated. This procedure was followed until the vapor pressure of the solution reached that of the saturated solution, thus enabling one to obtain several pressure readings in the more concentrated regions. The amount of ammonia withdrawn in each instance was determined by noting the temperature, volume and pressure, and the corresponding value was deducted from the total amount of ammonia present in order to obtain the true concentration of the solution. The process of withdrawing ammonia gas also served to remove small amounts of hydrogen that were present due to the formation of potassium amide. Although the amount of hydrogen formed in this reaction between ammonia and potassium was not great when the metal was free from its oxide, nevertheless, it was sufficient to produce a noticeable effect upon the total pressure readings in the highly concentrated solutions.

The measurements were carried out at three different temperatures, 0°, −33.5° and −50.38°. To maintain the temperature at 0°, the vapor-pressure tube was surrounded by a Pyrex Dewar flask containing finely-chipped ice in equilibrium with water. A thermometer calibrated by the Bureau of Standards was inserted into the bath and it was noted that the temperature remained at 0° ±0.05° for a period of several hours. A thin-walled tube was placed around the vapor-pressure tube in order to keep the potassium away from the ice-water mixture in case of accident.

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[1] Kraus and Lucasse: J. Am. Chem. Soc., **43**, 2529 (1921).

It was found more difficult to maintain constant temperature at the boiling point of liquid ammonia. The ammonia in the Dewar bath was allowed to boil against the atmosphere and the height of the liquid was kept as constant as possible by frequent additions. The atmospheric pressure was noted at frequent intervals during a determination. The variation in the temperature during a period of several hours was not greater than 0.1° under these conditions. The temperature was determined by noting at the beginning of a run the vapor pressure of pure liquid ammonia under the conditions to be followed in the course of the series of the measurements. The temperature corresponding to this pressure was then obtained from the tables given by Cragoe, Meyers and Taylor.[1] Four runs were carried out at the boiling point of liquid ammonia. The pressure of pure ammonia was measured in each case and found to be 755.0 mm., 754.4 mm., 752.8 mm. and 755.4 mm. respectively. The average value of these pressures corresponds to that of pure ammonia at a temperature of −33.5°. At this temperature the vapor pressure of pure ammonia changes approximately 38 mm. per degree; accordingly, the maximum variation in the temperature, as represented by the above pressures, is about 0.07°.

At −50° the temperature was controlled readily by boiling the ammonia in the Dewar bath under reduced pressure. An alcohol thermometer was placed in the bath, and, while a slow stream of hydrogen gas was allowed to bubble through the liquid for the purpose of maintaining uniform temperature conditions, the ammonia vapor was drawn off by means of a water-jet pump. The rate of evaporation was regulated by a screw clamp. The true temperature of the bath was determined by observing the vapor pressure of pure liquid ammonia when the thermometer reading was −50°. This pressure was found to be that of pure liquid ammonia at −50.38° according to the tables of Cragoe, Meyers and Taylor. The variation in the temperature throughout a series of measurements was not greater than 0.05°.

After a run had been carried out, the cooling bath was removed and the ammonia was allowed to escape. The potassium was then washed out of the vapor-pressure tube with ether, alcohol and, finally, water into a platinum dish. The greater part of the ether and alcohol was evaporated by warming and the alkaline solution was neutralized and acidified with hydrochloric acid. Finally, the solution was evaporated to dryness and the potassium chloride was heated to constant weight in a furnace at a temperature of 500°. The potassium was found to be free from iron and to contain only a minute amount of sodium. The ammonia used in the investigation was dried with metallic sodium and then distilled into a small steel cylinder.

Results

The results of four series of determinations at 0° are given in Table I; four series at −33.5° are given in Table II; and two series at −50.38° are given in Table III. The results obtained at 0° are plotted in Fig. 1, while

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[1] Cragoe, Meyers and Taylor: Bur. of Standards, Sci. Pub., 369, (1920).

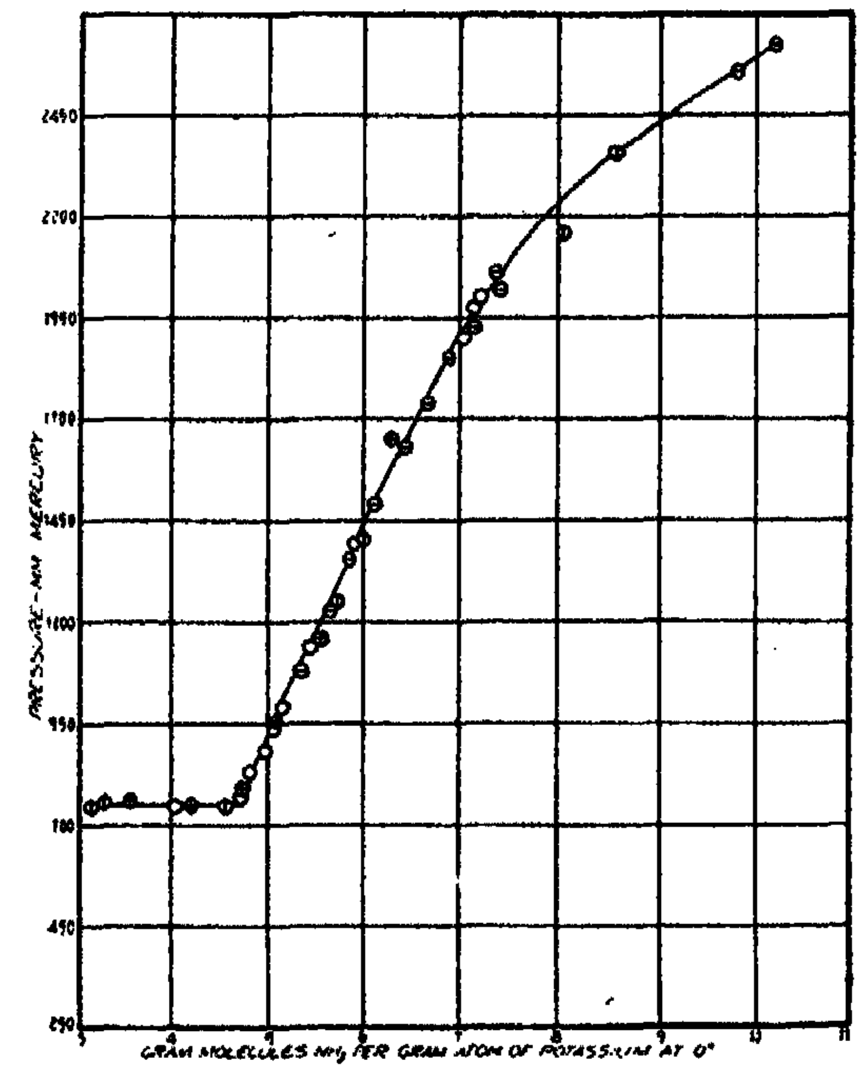
PRESSURE-MM MERCURY
2450
2200
1950
1700
1450
1200
950
700
450
200
3
4
5
6
7
8
9
10
11
GRAM MOLECULES NH3 PER GRAM ATOM OF POTASSIUM AT 0°

Fig. 1


PRESSURE-MM MERCURY
700
600
500
400
300
200
100
0
1
AT 33.5°
2
AT 50.38°
2
4
6
8
10
12
14
16
18
20
GRAM MOLECULES OF NH3 PER GRAM ATOM OF POTASSIUM

Fig. 2

those at the two lower temperatures are shown in Fig. 2. Many of the values are not plotted, especially in the concentrated regions, due to the overlapping of points. The concentrations are expressed in gram molecules of ammonia per gram atom of potassium; the pressures are given in millimeters of mercury.

The solubility of potassium in liquid ammonia, as determined by the extrapolation method outlined above, is given in Table IV. The values found by Joannis, Kraus and Lucasse and Ruff and Geisel are likewise listed in this table.

Table I

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at 0°

Series 1, 1.2818 g. of Potassium

Conc. NH_3/K	1.145	2.542	4.030	5.409	5.332	5.243
Press., mm.	748.3	755.9	748.9	1140.2	1082.5	1005.4
Conc. NH_3/K	5.147	5.050	4.956	4.701	4.615	5.880
Press., mm.	992.9	937.4	884.8	769.9	741.9	1393.6
Conc. NH_3/K	5.831	7.201	7.041			
Press., mm.	1356.1	2001.4	1901.9			

Series 2, 0.2806 g. of Potassium

Conc. NH_3/K	4.056	3.950	7.357	7.141	6.880	6.416
Press., mm.	799.5	753.3	2062.2	1975.1	1854.0	1632.0
Conc. NH_3/K	6.113	5.883	5.615	5.347	5.082	4.800
Press., mm.	1491.7	1354.9	1229.9	1091.2	965.2	832.8
Conc. NH_3/K	4.561	7.410	7.137	6.644	10.225	9.776
Press., mm.	760.1	2018.2	1927.6	1740.9	2623.4	2557.7

Series 3, 0.6501 g. of Potassium

Conc. NH_3/K	3.555	6.226	6.089	5.868	5.519	5.094
Press., mm.	764.4	1651.6	1501.5	1398.3	1161.5	959.2
Conc. NH_3/K	4.806	4.708	4.188			
Press., mm.	835.5	792.6	750.4			

Series 4, 0.4588 g. of Potassium

Cons. NH_3/K	3.260	3.123	5.999	5.692	5.394	5.098
Press., mm.	760.8	747.1	1405.7	1226.9	1070.7	918.3
Conc. NH_3/K	4.779	4.549	8.594	8.061	7.466	
Press., mm.	808.2	748.9	2360.5	2161.2	2018.8	

TABLE II

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at −33.5°

Series 1, 1.9412 g. of Potassium

Conc. NH_3/K	1.657	2.745	3.900	5.272	5.177	5.082
Press., mm.	165.0	163.5	167.0	208.0	191.0	177.2
Conc. NH_3/K	5.009	4.946	8.639	8.434		
Press., mm.	166.0	162.2	599.5	583.5		

Series 2, 1.5144 g. of Potassium

Conc. NH_3/K	2.386	3.773	3.695	5.188	5.084	4.984
Press., mm.	162.0	161.0	161.0	202.8	186.5	172.8
Conc. NH_3/K	4.877	6.193	8.431	8.274	10.576	10.437
Press., mm.	162.0	359.6	571.4	564.6	675.2	669.8
Conc. NH_3/K	13.077	12.470	15.231			
Press., mm.	722.5	707.2	732.3			

Series 3, 1.7333 g. of Potassium

Conc. NH_3/K	1.887	2.725	3.636	4.574	5.504	6.238
Press., mm.	159.7	159.5	161.6	166.2	294.5	396.2
Conc. NH_3/K	7.181	8.031	8.822	8.696	9.806	10.457
Press., mm.	500.3	566.9	615.0	601.2	640.5	666.3
Conc. NH_3/K	11.280	12.221	13.069	13.977	19.079	
Press., mm.	686.0	703.0	714.0	722.2	745.0	

Series 4, 0.8829 g. of Potassium

Conc. NH_3/K	2.134	4.429	6.581	6.331	6.007	5.714
Press., mm.	162.1	162.8	393.6	351.7	309.7	265.1
Conc. NH_3/K	5.462	5.248	5.067	4.899	6.682	8.352
Press., mm.	226.4	193.7	168.7	161.0	405.0	561.3
Conc. NH_3/K	10.228	12.792	12.096			
Press., mm.	657.4	711.8	693.6			

TABLE III

Vapor Pressure of Solutions of Potassium in Ammonia at Different Concentrations at −50.38°

Series 1, 1.1405 g. of Potassium

Conc. NH_3/K	1.485	3.686	5.269	5.200	5.131	5.062
Press., mm.	62.9	61.8	83.6	76.3	72.0	67.5
Conc. NH_3/K	5.006	6.895	8.801	8.609	10.264	11.900
Press., mm.	62.6	183.9	240.9	236.6	258.0	278.3

Series 2, 1.2304 g. of Potassium

Conc. NH_3/K	1.647	3.390	4.983	4.932	6.626	6.496
Press., mm.	63.4	63.5	64.8	62.6	174.4	166.4
Conc. NH_3/K	6.372	6.254	6.139	5.319	5.257	5.196
Press., mm.	159.1	152.3	145.2	81.2	76.6	72.0
Conc. NH_3/K	5.140	5.086	5.036	7.128	7.036	10.942
Press., mm.	68.7	64.6	63.6	193.2	187.9	276.5

TABLE IV

Solubility of Potassium in Liquid Ammonia

Temperature	0°	−33.5°	−50.0°	−100°
Johnson and Meyer	4.68	4.95	5.05	——
Joannis	4.31	——	——	——
Ruff and Geisel	4.74	——	4.79	4.82
Kraus and Lucasse	——	4.87	——	——

Discussion

The form of the vapor pressure curves for potassium dissolved in liquid ammonia corresponds closely to that of the curves for sodium and lithium. The vapor pressure of the solutions remains fixed as long as any potassium is present in equilibrium with the saturated solution. When solution of the potassium is complete, a marked increase in the vapor pressure is noticed as the concentration decreases. At still lower concentrations, the curves flatten out and approach the vapor pressure of pure liquid ammonia at the temperature in question. There are no breaks in the curve to indicate the formation of a compound between potassium and ammonia.

It will be noticed that the data given for the saturated solutions are not entirely consistent. This is due to the fact that in many instances the solutions were not allowed to come to equilibrium after each addition of ammonia, since, at these high concentrations, considerable time is required to establish true equilibrium conditions. The vapor pressure of the saturated solution was determined at each temperature independently and was found to have a value of 750 mm. at 0°, 162 mm. at −33.5° and 63 mm. at −50.38°. The first value is in agreement with that found by Joannis at 0°.

The data appear to be somewhat inconsistent at high concentrations where the curves are very steep. This is especially true at 0°. At this temperature, the vapor pressure changes approximately 250 mm. for a change in concentration of only 0.5 gram molecules of ammonia per gram atom of potassium. Hence, an appreciable change in pressure corresponds to a very small difference in concentration.

It is evident from the data given in Table IV that the solubility of potassium in liquid ammonia increases slightly with increasing temperature from −50.38° to 0°. At −50.38°, 100 grams of liquid ammonia dissolves 45.56 grams of potassium; at −33.5°, 46.38 grams of potassium; and at 0°, 49.05 grams of potassium. Ruff and Geisel also found that the solubility increases slightly with the temperature. The value given by these investigators for the composition of the saturated solution at 0° is 4.74 gram molecules of ammonia per gram atom of potassium, which is in good agreement with our value of 4.68. At −50°, the discrepancy in the results is much greater. It would appear that the value of 4.31 gram molecules of ammonia per gram atom of potassium given by Joannis at 0° is in error. Since he determined only two points at concentrations lower than that of saturation, it is difficult to conceive of an extrapolation possessing any significance.

Summary

The vapor pressures of solutions of potassium in liquid ammonia have been measured at 0°, −33.5° and −50.38° over a considerable concentration range.

The vapor pressures of the saturated solutions of potassium in ammonia at these temperatures are 750 mm., 162 mm. and 63 mm., respectively.

The solubility of potassium in liquid ammonia increases slightly with increasing temperature from −50.38° to 0°. The composition of the saturated solution, expressed in gram molecules of ammonia per gram atom of potassium, is 4.68 at 0°, 4.95 at −33.5 and 5.05 at −50.38°.

There is no evidence for the formation of a compound between potassium and ammonia.

SOLUTIONS FOR COLORIMETRIC STANDARDS. II. THE RELATION OF COLOR TO CONCENTRATION FOR AQUEOUS SOLUTIONS OF CERTAIN INORGANIC SALTS

M. G. MELLON

6.889

Judging from the lack of information, at least in chemical periodicals, regarding the use of numerical specifications of color, one is led to conclude that the average chemist, rather than having learned to think in these terms, is still attempting to specify colors descriptively, so that an object exhibiting a blue hue, for example, is designated simply as being a light, dark, medium, Alice, sky, azure, or some other type of blue.

Recently, two committees, composed of representatives from the various fields of activity interested in colorimetrics, published comprehensive reports describing methods of measuring and specifying colors[1, 2]. Following their suggestions, one may formulate a definite numerical specification of a given color on either the monochromatic or trichromatic system. The present paper is presented in the hope of aiding, in some small measure, the development among chemists of an appreciation of the possibility of applying these methods.

In the first paper of this series[3] data for various solutions were presented in the form of curves representing percent transmittancy as a function of wave length. The readings from which the curves were constructed had been obtained by determining, at the wave lengths indicated, the percent of incident light transmitted by the various solutions, relative to that transmitted by the pure solvent. Such curves, in themselves, may be sufficient for certain purposes as an indication of the properties of the system measured; but in case one wishes to know the relative brilliance, colorimetric purity (saturation), and dominant wave length of the system, or the percentages of elementary red, green, and violet excitations constituting the color, further calculation is necessary. An example is given below of how this is done for a given solution, together with the collected data for several solutions of different concentrations.

Method of Calculation

The data presented here were all determined by means of calculations based on the curves previously published, and include only the inorganic solutions of Arny mentioned in the first paper.

An inspection of the original curves, involving measurements made with a Keuffel and Esser spectrophotometer, indicates that the readings did not cover the whole range of wave lengths from 400 to 700 mμ, due to the fact that the relative visibility for different wave lengths becomes quite low toward either the red or violet end, rendering the readings in these regions

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[1] Troland et al.: J. Optical Soc. America-Rev. Sci. Instruments, 6, 527 (1922).

[2] Gibson et al.: J. Optical Soc. America-Rev. Sci. Instruments, 10, 169 (1925).

[3] Mellon and Martin: J. Phys. Chem., 30, 161 (1927).

too uncertain to be very reliable. However, in making calculations, such as those presented below, one can scarcely neglect the effect of the violet excitations for wave lengths below 440mμ, where readings on the Keuffel and Esser instrument are difficult to make. It is necessary, therefore, to extrapolate the curves previously presented in order to include the whole region between 400 and 700 mμ. An inspection of the published curves indicates that, in some instances at least, such an extrapolation becomes a little too much of a guess to leave one entirely comfortable; but, on the other hand, failure to make such extrapolations, which finally involves the omission of certain elementary color excitations (particularly serious in the violet region), leads to absurd results when one attempts to construct a curve coördinating some given value with concentration for a solution such as cobaltous chloride.

In order to indicate just what was done in this direction before calculating the present data, there is included in Table I the value of the transmittancies which it seemed might reasonably be used as extrapolated values for the ends of the curves.

Since the method for calculating the values used in specifying a color seem not to be generally known, illustrative calculations have been made for an ammoniacal solution of cupric sulfate having a concentration of two hundredth molar. The following steps indicate the general procedure involved:

1. Extrapolate (if necessary) the spectral transmission curve, as described above, constructed from the two sets of values read directly on the Keuffel and Esser color analyzer. For the solution of cupric sulfate these values (wave length and percent transmittancy) are given in columns 1 and 2 of Table II.

2. Obtain, by means of the special slide rule available for the Keuffel and Esser spectrophotometer, at intervals of even 10 mμ, the values given in columns 3, 4, 5, and 6 of Table II; that is, calculate the elementary color excitation values for red, green, and violet and the value of the relative brilliance. With considerable more effort, these values may be calculated without the special slide rule.[1]

3. Obtain the sum of the values in each of columns 3, 4, and 5. Then reduce these sums to percentage form by dividing the sum for each column by the sum of all three. Multiplying the results by 100 gives the percents of red, green, and violet.

4. Obtain the dominant wave length and the percent colorimetric purity by means of the color triangle available for such work, using the percents of red and violet calculated above.

5. Obtain the sum of the values in column 6 and divide by the sum of the luminosity values for "average noon-day sunlight" (10.6856)[2] in order to calculate the percent relative brilliance.

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[1] Ferry: "Physics Measurements", 1, 239 (1926).

[2] See Ref. 2, Table VI.

TABLE I

Values used for percent transmittancy for the ends of curves for various solutions (extrapolated if necessary)

Solution	Concn.	Violet End	Middle	Red End
$CuSO_4$	M/4	100 at 470mμ		1 at 623 mμ
	M/8	" " "		" " 660
	M/16	" " 500		" " 700
	M/32	" " "		8 " "
$Cu(NH_3)_4SO_4$	M/100	100 at 430		1 at 548
	M/200	" " "		5 " 700
	M/400	" " 440		30 " 700
$(NH_4)_2CrO_4$	M/300	1 at 457		100 at 510
	M/600	" " 440		" " "
	M/1200	" " 428		" " 500
$FeCl_3$	M/4	1 at 486		66 at 700
	M/8	" " 470		89 " "
	M/16	" " 453		96 " "
	M/32	" " 440		100 " 610
$Co(NH_3)_6Cl_3$	M/100	100 at 410	1 at 450 " " 550	100 at 700
	M/200	" " "		" " 680
	M/400	" " 420		" " 630
$CoCl_2$	M/4	100 at 400	1 at 450 " " 558	71 at 700
	M/8	" " "	1 " 470 " " 540	76 " "
	M/16	" " 410		87 " "
	M/32	" " 420		98 " "
$K_2Cr_2O_7$	M/6	1 at 548		100 at 590
	M/12	" " 540		" " 585
	M/60	" " 522		" " 575
	M/300	" " 492		" " 570
	M/600	" " 473		" " 550

TABLE II

Colorimetric data for a two hundredth molar solution of tetrammino-cupric sulfate

Wave length	T	Elementary color excitation values			Relative Brilliance	Wave length × Rel. Bril.
		Red	Green	Violet		
400 mμ	100%	——	——	29.60	——	——
410	100	——	——	33.70	——	——
420	100	——	——	51.20	——	——
430	100	——	——	81.40	0.0119	5.12
440	97	——	0.65	93.00	0.0168	7.39
450	87	——	1.39	81.40	0.0259	11.66
460	78	——	3.10	67.50	0.0370	17.03
470	68	——	5.95	50.30	0.0528	24.82
480	59	0.91	8.02	30.60	0.0750	36.00
490	49	2.26	9.45	12.10	0.0998	48.92
500	39	3.72	11.80	5.50	0.1230	61.47
510	28.6	5.03	13.20	2.89	0.1440	73.40
520	19.7	5.40	12.00	1.41	0.1360	70.68
530	13.6	4.96	9.39	0.70	0.1150	60.92
540	9.6	4.27	7.02	0.33	0.0928	50.10
550	7.0	3.54	5.20	0.15	0.0698	38.40
660	5.1	2.83	3.56	0.07	0.0503	28.16
570	3.8	2.28	2.36	0.03	0.0358	20.41
580	2.9	1.78	1.44	0.01	0.0251	14.56
590	2.4	1.50	0.84	——	0.0179	10.56
600	2.1	1.24	0.48	——	0.0129	7.74
610	2.0	1.05	0.26	——	0.0097	5.92
620	2.0	0.83	0.13	——	0.0072	4.46
630	2.2	0.68	0.07	——	0.0054	3.40
640	2.4	0.50	0.03	——	0.0038	2.43
650	2.7	0.34	0.01	——	0.0025	1.62
660	3.1	0.22	——	——	0.0014	0.92
670	3.6	0.14	——	——	0.0008	0.53
680	4.0	0.09	——	——	0.0004	0.27
690	4.6	0.06	——	——	0.0004	0.27
700	5.1	0.06	——	——		
		43.69	96.35	541.89	1.1732	607.05
Dom.λ	Purity					
468mμ	50%	6.4%	14.1%	79.5%	11.0%	517.4 mμ

6. To calculate the values in column 7 multiply each wave length indicated by the corresponding value for relative brilliance. The sum of these values is then divided by the sum of the values for relative brilliance to obtain the wave length of the spectral centroid (or center of gravity).

Having made such a set of calculations, the color then may be definitely specified by giving, for the trichromatic system, the percents of red, green, and violet, or, for the monochromatic system, the percents colorimetric purity and relative brilliance, together with the dominant wave length.

Having made such a calculation, it should be kept in mind, however, that the colorimetric specification so obtained holds only when the object is illuminated by "average noon-day sunlight." Similar calculations can be made, of course, for other sources of illumination, providing one knows their spectral distribution curves. The special slide rule would not be applicable then, since its values are based on determinations for average noon-day sunlight.

Relation of Color to Concentration

If one were to inquire of most chemists what happens colorimetrically on adding more solvent to a given colored solution, they would probably reply that the process of dilution renders the color paler or less intense. Similarly, the more concentrated of two colored solutions is frequently referred to as having the deeper color. In view of the newer specification of color, such an answer is not entirely satisfying; one is led to seek the effect of dilution on the various numerical values, or, in general, the relation of color to concentration.

Since the curves previously published had been determined for several concentrations, it seemed worth while to make the necessary calculations for them. Accordingly, the data were compiled for aqueous solutions of cobaltous chloride, ferric chloride, and cupric sulfate, all acidified with hydrochloric acid, for ammoniacal solutions of tetrammino-cupric sulfate and chloro-pentamminocobaltic chloride, and for an aqueous solution of potassium bichromate. The calculated values[1] are given in Table III.

In order to show a little more clearly the relationships involved, an attempt has been made to construct curves coördinating the various colorimetric values with the concentration of the solutions. Being unable to read precisely in the red and violet regions of the spectrum, thus necessitating certain extrapolations for the original curves, introduces an undesirable uncertainty into the calculated values; but it seems probable that they have a reasonable reliability in indicating the general direction of the effect of dilution upon the various numerical colorimetric values. Preferably, also, a greater number of dilutions should have been included; but when the measurements were made, the present calculations were not contemplated and the limits of concentration used were determined largely by the difficulty of obtaining reproducible readings for the transmittancy. Curves for the seven solutions

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[1] It should be pointed out, perhaps, that the colorimetric analysis of the two solutions of the cobalt salts shows that each has a purple hue. Such a color does not have any real dominant wave length; that is, one cannot find any mixture of homogeneous light and "white light" which will match the purple color. When giving the monochromatic specification in such a case, one conventionally and conveniently specifies the complementary's dominant wave length. This is defined as the wave length of the light which is required to be mixed with the sample light in order to match white. Consequently, the hue so obtained, instead of being like that of the sample, is farthest removed from it.

TABLE III

Numerical specifications of color for different solutions

Solution	Concn.	Trichromatic analysis			Monochromatic analysis			Spectral Centroid
		Red	Green	Violet	Rel. Br.	Dom. λ	Purity	
$CuSO_4$	M/4	17.2%	30.3%	52.5	44.7%	485mμ	44%	533.2 mμ
	M/8	21.4	32.1	46.5	56.7	486	32	541.7
	M/16	26.0	33.6	40.4	73.1	488	22	548.4
	M/32	28.7	33.5	37.8	81.0	488	15	552.9
$Cu(NH_3)_4SO_4$	M/100	1.8	7.3	90.9	4.0	462	75	491.1
	M/200	6.4	14.1	79.5	11.0	468	50	517.4
	M/400	16.9	24.0	59.1	30.7	474	25	540.8
$(NH_4)_2CrO_4$	M/300	47.2	45.3	7.5	94.4	572	84	562.6
	M/600	45.4	44.2	10.4	95.2	572	76.5	561.8
	M/1200	43.1	42.5	14.4	96.1	571	66	561.8
$FeCl_3$	M/4	53.8	44.1	2.1	53.2	579	96	570.9
	M/8	51.2	45.3	3.5	68.2	576	93	567.0
	M/16	48.7	44.8	6.5	83.6	574.5	86	564.9
	M/32	46.1	43.6	10.3	90.4	573	77	563.5
$Co(NH_3)_5Cl_3$	M/100	53.4	13.6	33.0	12.6	496.5C	58.5	613.2
	M/200	45.5	19.7	34.8	26.7	497.6	47	595.7
	M/400	40.1	25.1	34.8	46.1	498.3	33	580.9
$CoCl_2$	M/4	54.6	18.5	26.9	11.5	494C	52	605.3
	M/8	52.8	23.2	24.0	22.2	492.3	43	598.1
	M/16	43.9	24.5	31.6	36.3	495.3	37	587.6
	M/32	38.5	27.2	34.3	52.5	498	27	576.7
$K_2Cr_2O_7$	M/6	69.4	30.4	0.2	39.2	597	100	597.8
	M/12	66.8	32.9	0.3	44.7	592	100	593.9
	M/60	60.3	39.0	0.7	60.7	587	99	583.3
	M/300	55.6	43.0	1.4	74.4	581.5	97.5	574.5
	M/600	52.9	44.8	2.3	82.8	579	95	569.8

C—Dominant wave length of complementary

whose values have been calculated are shown in Figs. 1-4, the abscissas being the reciprocal of the molar concentration (on a logarithmic scale) and the ordinates being percent for relative brilliance, colorimetric purity, and elementary excitation values, and wave length (in millimicrons) for dominant wave length and spectral centroid.

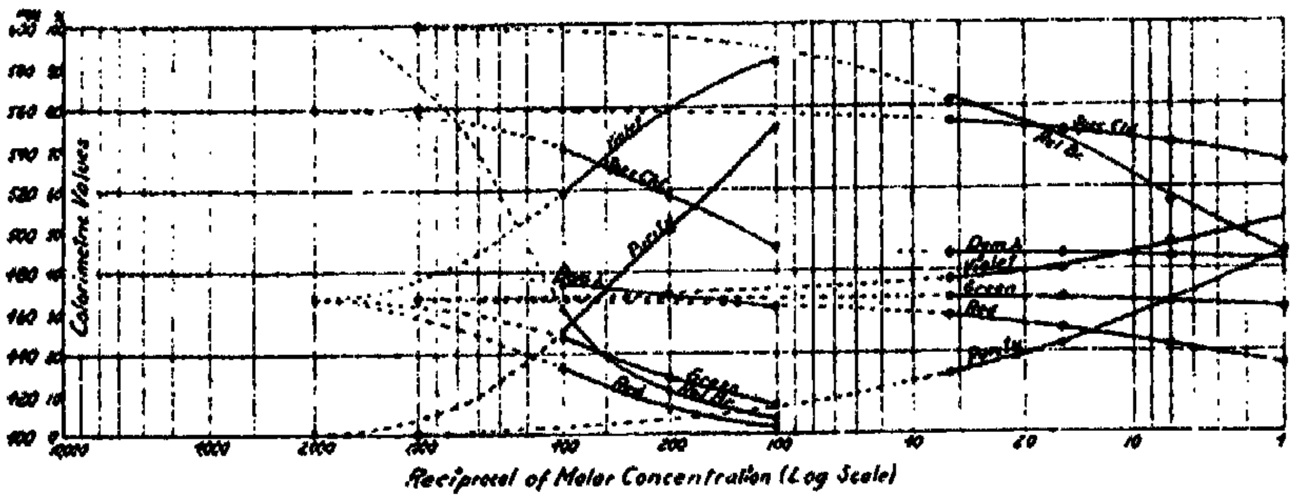

FIG. 1

Curves showing the various colorimetric values for different concentrations of an acidic (circles) and an ammoniacal (crosses) solution of cupric sulfate.

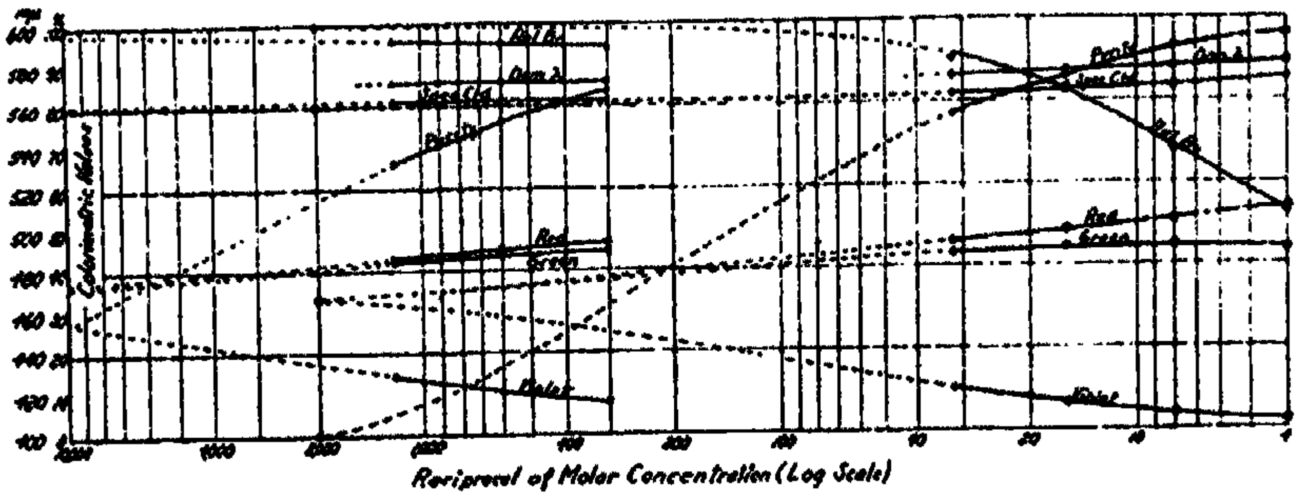

FIG. 2

Curves showing various colorimetric values for different concentrations of an acidic solution of ferric chloride (circles) and an ammoniacal solution of ammonium chromate (crosses).

Although the readings for the original transmission curves were carried about as far in dilutions as was consistent with obtaining fairly dependable values, the construction of the present curves raised the question of where they would extend when the solution no longer exhibited any color, or, ultimately, when the concentration of the solute reached zero. Accordingly, the venture of extrapolating the curves was made. This again involves some uncertainty regarding the exact position of the curves; but the final values for zero concentration seem pretty definite, and were assumed to have the following values: relative brilliance, 100%; colorimetric purity, 0%; spectral centroid for equal energy spectrum and visibility, 560.2 mμ[1]; red, green, and violet excitations, 33⅓%; and dominant wave length, indeterminate.

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[1] Calculated from data in Table VI, Ref. 2.

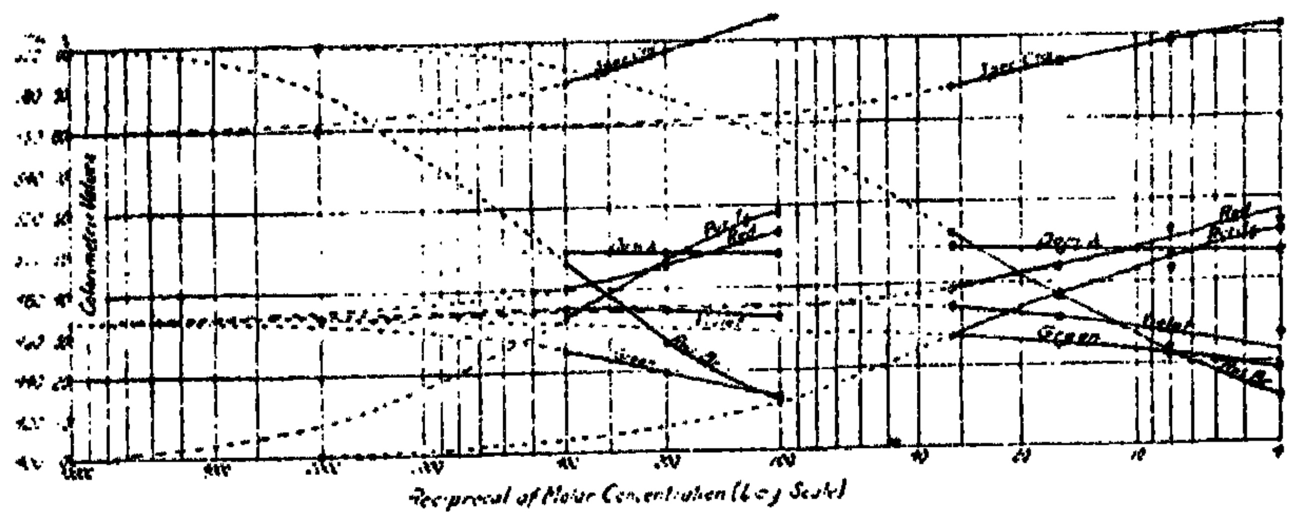

Fig. 3
Curves showing various colorimetric values for different concentrations of an acidic solution of cobaltous chloride (circles) and an ammoniacal solution of chloro-pentammino-cobaltic chloride (crosses).

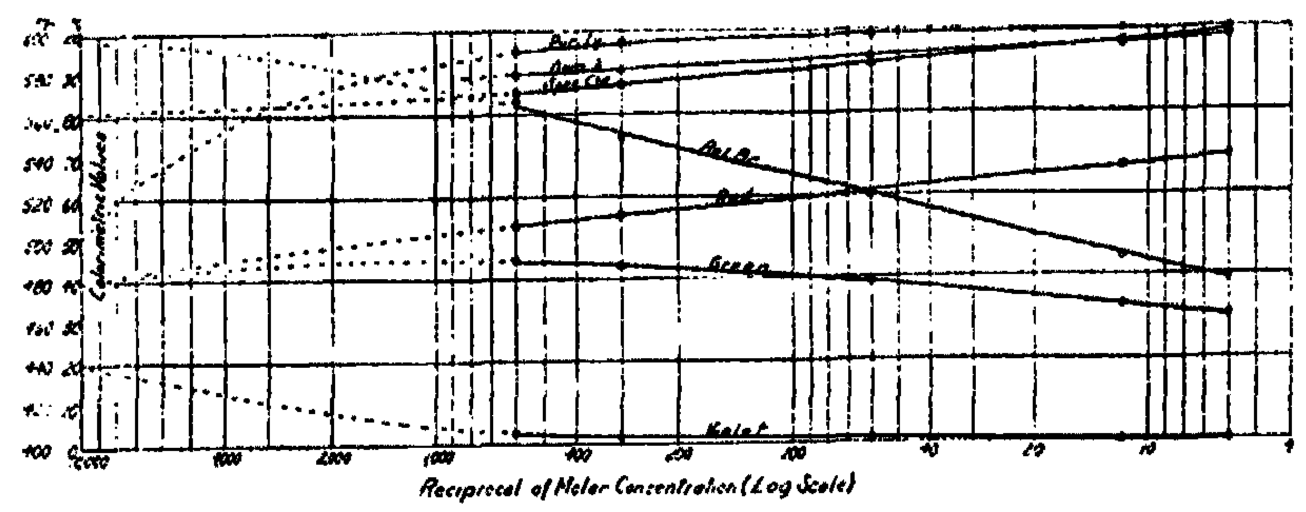

Fig. 4
Curves showing various colorimetric values for different concentrations of an aqueous solution of potassium bichromate.

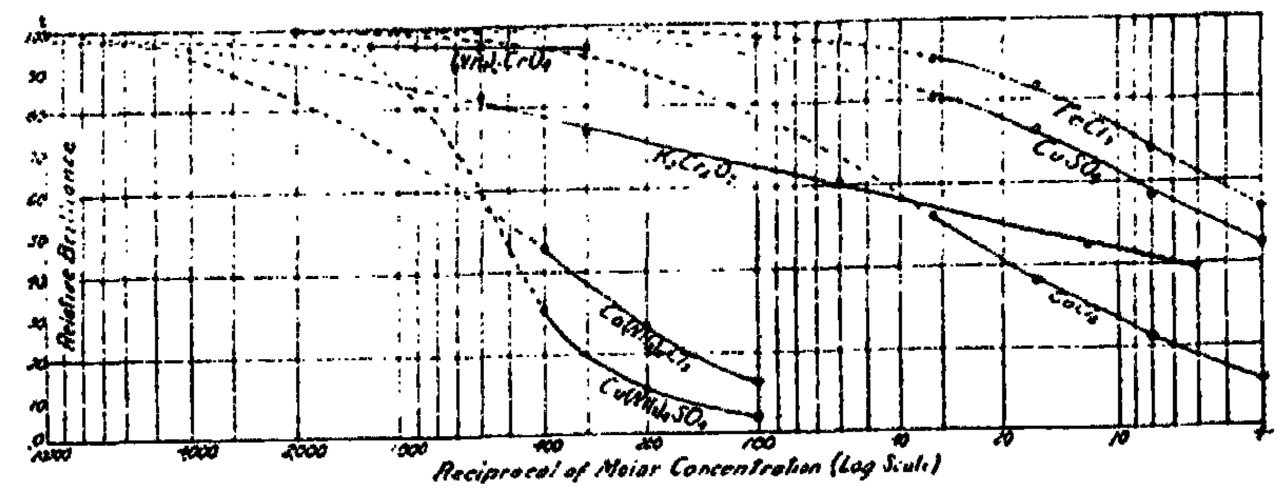

Fig. 5
Curves showing values for relative brilliance of various solutions of different concentrations.

Strictly speaking, the approach of the curves toward the horizontal lines running through the above values for zero concentration should be asymptotic. Instead of attempting to extrapolate to zero concentration, however, it was assumed that, practically, one is not greatly concerned with dilutions beyond the point where color is no longer distinguishable. In order to determine this "vanishing point" of the color, dilutions were made until 20 ml. of the solution practically matched an equal volume of distilled water when compared in the long type of Nessler tubes. The values thus determined are indicated as the final points for all curves except in the case of potassium bichromate and ammonium chromate, where it was approximately fifteen thousandth molar.

In Fig. 5 there is included a set of curves to show, for the seven different solutions, the relation of one colorimetric value, relative brilliance, to the concentration of the solutions. Such a comparison, for either the acidic or basic set of solutions, is of interest in view of Arny's statement that the concentrations selected by him (fourth molar, for example, for the acidic set) were such as to give solutions whose "depth" of color was about the same. A similar set of curves for colorimetric purity shows wide variations for the different solutions.

Conclusions

It has already been pointed out that the data presented here must be considered as only approximately quantitative on account of the small number of dilutions involved and the necessity of making certain extrapolations for the portion of the data not obtainable from the original measurements. The latter procedure, however, is the one recommended by the manufacturers for the instrument used. Keeping these limitations in mind, the following items are suggested as the presentations of this paper:

1. Typical data involved in the calculations of the numerical specification of a color on either the monochromatic or trichromatic system.

2. Data showing the general relationship of the color of certain solutions, as specified numerically, to their concentration. The following summary indicates, for the seven solutions studied, the direction of the effect of dilution on each of the seven values calculated:

a. Elementary excitation values
  a. Red: increase, if hue is blue; decrease, if hue is yellow, orange, or purple.
  b. Green: increase, if hue is blue,[1] orange, or purple; decrease, if hue is yellow.
  c. Violet: increase, if hue is yellow, orange, or purple;[2] decrease, if hue is blue.

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[1] Questionable in case of acidic solutions of cupric sulfate.

[2] Questionable in case of chloro-pentammino-cobaltic chloride.

b. Dominant wave length: increase, if hue is blue or purple (λ of complementary); decrease, if hue is yellow or orange.

c. Spectral centroid: increase, if hue is blue; decrease, if hue is yellow, orange, or purple.

d. Relative brilliance: increase, for all hues.

e. Colorimetric purity: decrease, for all hues.

The author gladly acknowledges his indebtedness for valuable suggestions from Mr. F. D. Martin, a former student, and from Mr. I. G. Priest of the U. S. Bureau of Standards.

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ON THE IONIZATION PRODUCED IN THE OXIDATION OF NITROGEN DIOXIDE

BY LOUIS A. M. HENRY

Introduction

In the study of the dynamics of electrons in chemical reactions, it is interesting to know whether the homogeneous gaseous reaction is accompanied by the liberation of electric charges, resulting in a production of ions. Besides much preliminary work,[1] the question was studied very carefully by A. Pinkus,[2] and quite recently by A. K. Brewer.[3] In the case of the oxidation of nitric oxide by oxygen, the results of Pinkus were absolutely negative. Brewer found at 385° a very definite positive and negative ionization, although the results were not very reproducible at room temperature and 100°C. Brewer attributed these difficulties principally to an adsorption of N_2O_4 by the metallic electrodes. The reaction of nitrogen oxide with oxygen is studied again in this work, the purpose of which is to investigate, as carefully as possible, the effects at low temperatures. These are interesting because of the negative coefficient of temperature of the reaction velocity constant,[4] and of the difficulty of finding a satisfactory molecular structure[5] for NO_2.

Principle of the Method

Into a suitable ionization chamber of glass, quartz and platinum, are conducted well-controlled streams of O_2 and NO. O_2 was always in such an excess as to assure a complete oxidation of NO *in the chamber*. From the data obtained, it is possible to calculate the number of reacting molecules per second (m); and from the intensity of the ionization current, the number of ions captured per second (n): hence the ratio n/m.

In all this work, great care was taken to use gases as pure and dry as possible. For this purpose, all the parts of the apparatus were fused together; every part was cleaned with cleaning solution and distilled water. The stopcock grease was boiled a long time in contact with the reacting gases, to avoid all attack and production of moisture.

The Gases

Oxygen: was generally prepared by the action of water on sodium peroxide. The possible traces of O_3 were destroyed by bubbling through mercury. The gas was stored in a 10 liter gasholder. From there to the reaction cham-

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[1] For this bibliography cf. A. Pinkus: J. Chim. phys., **21**, 71 (1924).

[2] A. Pinkus: J. Chim. phys., **16**, 201 (1918); **18**, 412 (1920).

[3] Brewer: J. Am. Chem. Soc., **46**, 1403 (1924); Brewer and Daniels: Trans. Am. Electrochem. Soc., **44**, 171 (1923).

[4] Bodenstein: Z. physik. Chem., **100**, 68 (1922).

[5] A brief account of this work has been published; cf. A. Pinkus and L. Henry: Bull. Soc. chim. Belge, **37**, 285 (1928).

ber, the oxygen passed through a tube of granulated potassium hydroxide, a bubbler of concentrated H_2SO_4 and two tubes of P_2O_5.

For the very rapid flows, oxygen from a tank was stored in a 60 liter gasholder. From there, it passed through two long tubes of graulated potassium hydroxide, two H_2SO_4 bubblers of two liters capacity, followed by a tube containing glass wool. It was finally dried by passing through six tubes of phosphorus pentoxide.

Nitrogen Dioxide: was prepared by the action of dilute H_2SO_4 on a 20% sodium nitrite solution. From the gasholder, the gas passed through granulated KOH, bubblers of concentrated H_2SO_4 (solution of higher nitrogen oxides); and finally through two tubes of P_2O_5.

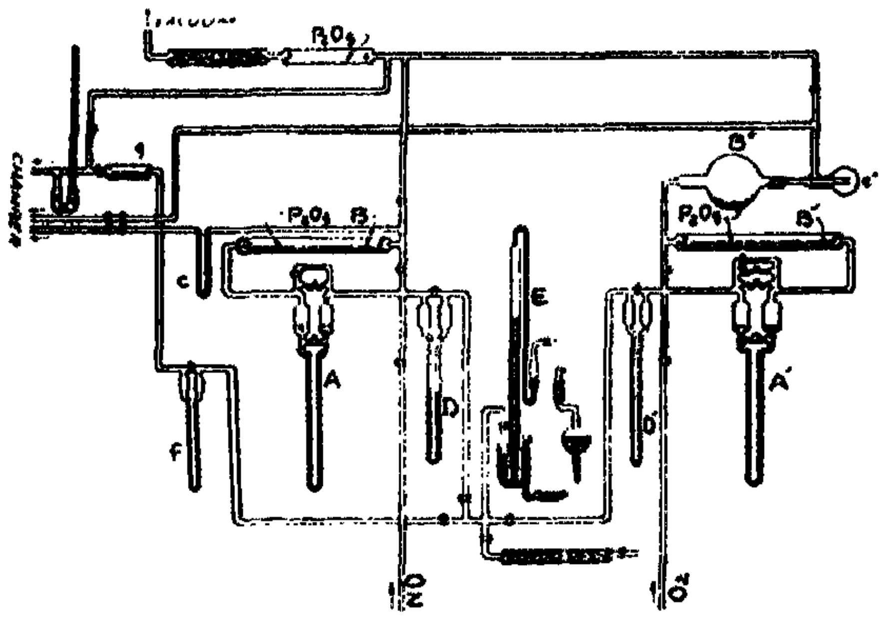

FIG. 1

Measurements of the Rates of Flow and Pressures of the Gases

The flows of gases are measured by two very sensitive flowmeters (A and A′, Fig. 1) the principle of which is well known;[1] a series of shunts allowed the measurement of flows from 50 cc to 40 liters per hour with a precision of 0.2%. They were calibrated by sending through them variable streams of gases which were received in a graduated burette over water kept saturated with the gas, or over mercury. The pressure of the gas at the entrance of the flowmeters is always the pressure of calibration. It is measured by the barometer E, and controlled at any time by the differential manometers D and D′ (filled with phosphoric acid). In this way the pressure was kept constant at less than a tenth of a mm of mercury.

In these flowmeters and manometers, the gases are only in contact with H_3PO_4, and their perfect desiccation is assured by passing them again over P_2O_5 in B and B′ (and in the bulb B″ for the high flows of O_2).

Glass wool at the end of the drying tubes, the capillary C′ and the bulb C″ prevent the dust from coming into the chamber.

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[1] A. Pinkus and A. Juliard: J. Chim. phys., **24**, 374 (1927).

Ionization Chambers

After many trials, three ionization chambers were used, designated as chambers I, II, III.

Chamber I: It consists of a Pyrex tube. One of the electrodes is a very thick layer of platinum (a) deposited on the inner part of the tube by reduction of chloroplatinic acid[1] and connected to the high-voltage battery by a platinum wire (f) sealed in the glass.

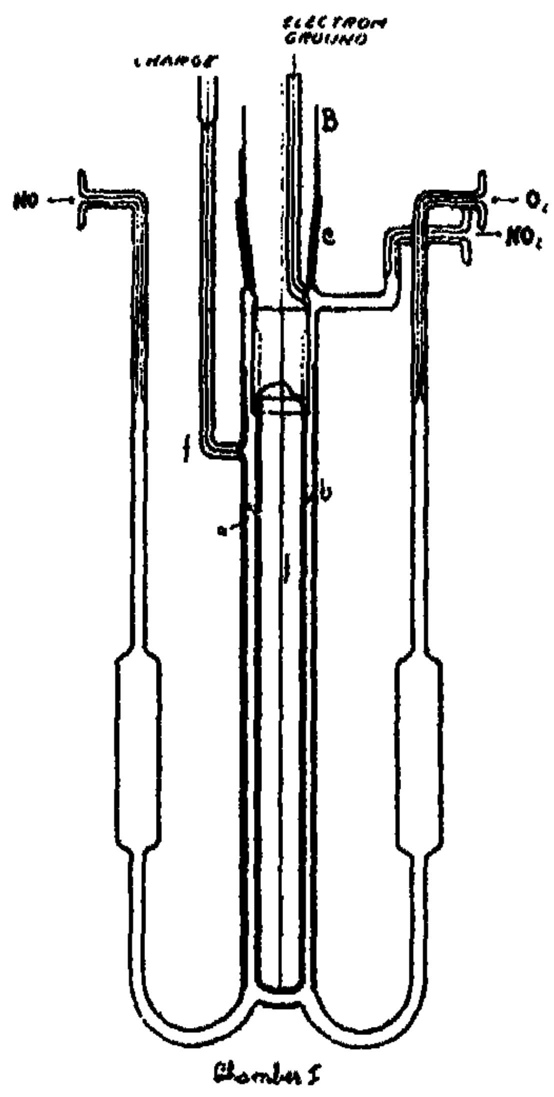

Fig. 2

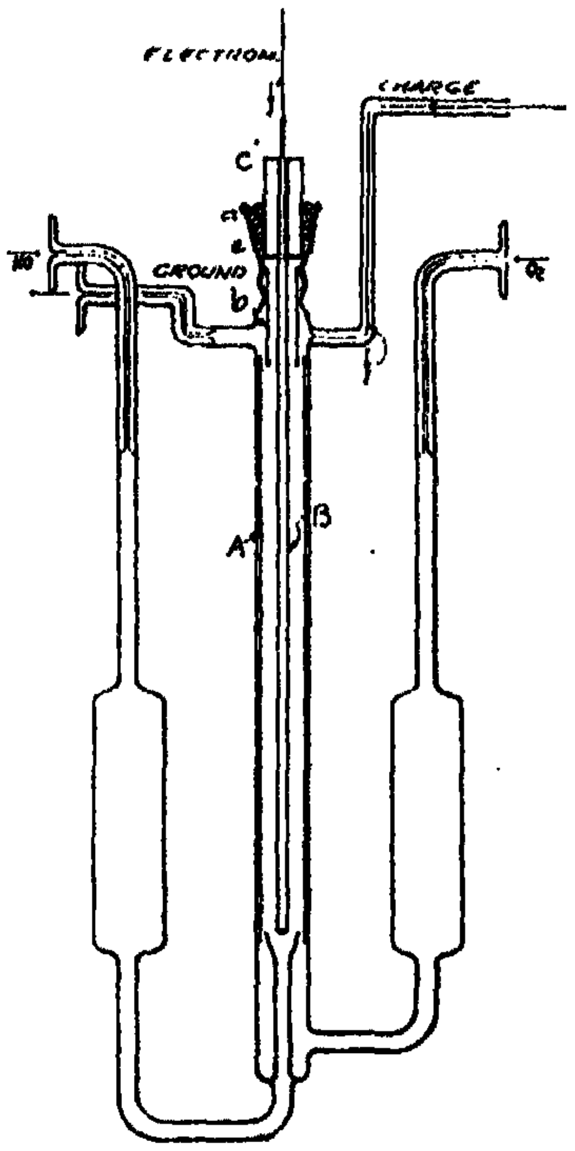

Fig. 3

A ground joint (C') supports an inner Pyrex tube (B) externally platinized. The platinum layer (b) is connected to the electrometer by a wire f' sealed in the glass. At the top of (B) a length of 2 cm is free from platinum to assure a good insulation of (b), and is protected by a Faraday screen (platinum cylinder). The ground joint is platinized and grounded, to avoid the transfer of electricity from (a) to (b) over the surface of the glass. The two electrodes are 0.5 cm apart from each other, their electrical capacity is 19.8 cm. The tubes E and F introduce the gases at the bottom of the chamber, the tube G takes them out at the top.

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[1] After many trials, the best results were obtained with a mixture of chloro-platinic acid and lavendar oil. Camomillia oil gives a very bright mirror, but not so resisting.

This chamber was very satisfactory at low temperatures, but at higher temperatures the Pyrex did not insulate very well and a great deal of trouble occurred, due probably to the electrification or electrolysis of the glass.

Chamber II: (Fig. 3): It consists also of a Pyrex tube, but the electrodes A and B are of massive platinum, and the insulation is assured by a transparent quartz rod (C). The electrode A is a platinum cylinder, fitting exactly in the tube. It is connected to the battery by a wire (f). The electrode (B) is a platinum rod supported by the quartz rod (C). It is connected to the electrometer by the wire (f′). The neck of the chamber is platinized and grounded to make a guard ring (a). A platinum cylinder (b) acts as a Faraday screen between (B) and all free parts of glass. The chamber is perfectly closed by a thin layer of Golaz mastic.[1] This is cooled in the experiments at high temperature by a copper jacket with circulating water.

Chamber III: It is very similar to chamber II, but is closed by a quartz ground-joint avoiding all sealing; it was used in the last experiments.

These chambers are heated in an electric furnace, each part being immersed in iron filings. Since the introduction of cold gases in the chamber sometimes produced trouble, they were heated in the thermostat. Above 100°C they were preheated in special furnace to insure the equality of their temperature with that of the chamber.

The pressure in the chamber is measured by means of a barometer E (Fig. 1) and the phosphoric acid manometer (F) insulated from the chamber by a P_2O_5 tube (G). The gases are drawn out of the chamber by a water pump, insulated from the chamber by drying tubes. The variations in water pressure are compensated by allowing variable amounts of air to pass through a bubbler.

Since the chamber is separated from the rest of the apparatus by drying tubes, the gases are perfectly dry at the time of the reaction. They are only in contact with glass, quartz, and platinum, avoiding the accessory phenomena such as attack of the insulators.

Electrical Apparatus (Fig. 4)

A Lindemann[2] electrometer was used throughout the whole work. (A Wilson electrometer was constructed to check the measurements, and gave exactly the same results.) The quadrants are charged at ±20 volts by two batteries of Weston cadmium cells. On adjusting accurately the potential by the potentiometer system (C) a sensitivity from 100 to 1000 eyepiece divisions per volt was obtained. The sensitivity was frequently checked by the potentiometer J and the Weston standard cell Q.

The needle of the electrometer is connected (a to the central electrode of the ionization chamber; b) to the (E) plate (quartz insulated and with guard ring) of a 3 cm capacity condenser. The other plate of this condenser (F) could be charged to a variable potential by the potentiometer (H, G) for compensation measurements. Three electromagnetic keys (L_1, L_2, L_3) were

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[1] This mastic is more elastic than sealing wax, and not so soft as the picein.

[2] Lindemann: Phil. Mag., 47, 578 (1924).

used to ground the whole system, connect the electrometer to the charging system (J) or to the Wulf's standard condenser (K). In any case, the whole electric capacity of the system was more than 50 cm. All connections were made of copper wire supported by quartz rods in wide copper tubings. These were perfectly tight and dried with phosphorus pentoxide. High voltage was supplied by a 2000-volt storage battery, running continuously on a high resistance, giving a very steady source of potential, even for experiments in which the electrometer remains insulated for three or four hours.

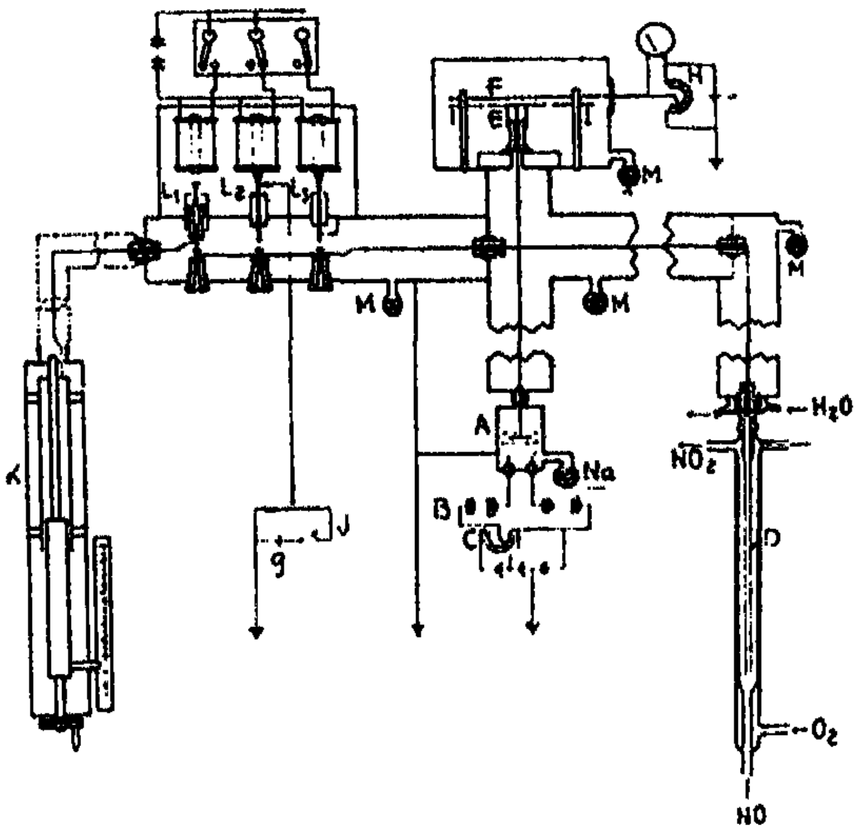

Fig. 4

Experimental Method

Before each experiment the chamber is evacuated with a water pump, an oil pump, and finally a known flow of O_2 is passed through it. The external electrode being charged, the needle of the electrometer is insulated, and its motion observed. The NO is then introduced simultaneously with O_2, the motion of the needle being always observed. Thus it is possible to plot a curve: variation of the potential of the needle against the time; the first part of the curve corresponding to the flow of pure O_2, the other to the flow of the mixture $NO + O_2$. Besides this method, the Bronson[1] compensation method was used.

Ionization Calculation

First Method: If "c" be the electrical capacity of the whole apparatus connected to the needle of the electrometer: "Dv" the variation, in volts, of its potential in a time "t" seconds; the intensity "i" of the ionization current may be expressed:

$$i = \frac{c \cdot Dv}{t} \text{ amperes.} \qquad (1)$$

But 1 amp. = 3.10^9 e.s.u. and 1 elementary charge = $4.8\cdot10^{-10}$ e.s.u., so that

$$i = \frac{3.10^9}{4.8\cdot10^{-10}}\cdot\frac{c\cdot Dv}{t} = 6.3\cdot10^{18}\,\frac{c\cdot Dv}{t}\ \text{elementary charges per second.} \tag{2}$$

The intensity of the ionization corresponding to the second part of the curve (mixture $NO + O_2$), must be corrected for the ionization occurring in O_2 alone. If for a time interval "t," the potential variation in O_2 alone is Dv′ and in $O_2 + NO$ is Dv, the true value of the ionization in the reacting mixture will be

$$i(\text{correct.}) = \frac{c}{t}\,(Dv - Dv')\ \text{amps} = \frac{6.3\cdot10^{18}}{t}\,c\cdot(Dv = Dv')\ \text{elem. charges sec.} \tag{3}$$

Practically, Dv′ may always be neglected.

The first method, which was generally used, necessitates the continuous observation of the electrometer for several hours. But it has the advantage of giving a good representation of the whole phenomenon.

2) *Compensation Method:* As the insulated needle accumulates by ionization charges which increase its potential, these charges are continuously neutralized by inducing on the plate E of the compensating system, a variable charge of opposite sign. So the needle is kept to the zero.

If "c" is the capacity of the compensating condenser; V_1 in volts the initial potential of the plate E, V_2 is the potential after t seconds, the intensity of the ionization current "i" is expressed:

$$i = \frac{c't}{t}\,(V_2 - V_1)\ \text{amps.} = 6.3\cdot10^{18}\,\frac{c'}{t}\,(V_2 - V_1)\ \text{elementary charges sec} \tag{4}$$

Sensitivity of the Electrical Apparatus

The electrometer was frequently used with a sensitivity of 100 eyepiece divisions per volt. The total electrical capacity was never more than 50 cm ($5.5\cdot10^{-11}$ farads). If one considers the limit of measurable motion of the needle to be 1 division in 10′ (which was possible owing to the very good stability of the high voltage battery), then by introducing those values in eq. (3) the limit of measurable current will be:

$$i = \frac{5.5\cdot10^{-11}\cdot10^{-2}}{6\cdot10^2} = 9\cdot10^{-16}\ \text{amps.}$$

Using the compensation method, the capacity c′ being $3.3\cdot10^{-12}$ farads, a variation of the potential of the compensating condenser of 0.1 v. in 10 minutes corresponds to an ionization current of:

$$i = \frac{3.3\cdot10^{-12}\cdot10^{-1}}{6\cdot10^2} = 5.5\cdot10^{-16}\ \text{amps.}$$

In verification experiments, with pure oxygen, the electrometer was frequently used with a sensitivity of 1000 eyepiece divisions per volt. In this case a current of 10^{-16} amps. can be measured.

Experimental Results

Experiments below 100°C.

A first series of experiments was made with chamber 1. Temperature = 20°C; potential gradient between the electrodes = ±1000 v; flows of O_2 and NO of about 1 liter per hour. Preliminary experiments were made with O_2 and NO alone, and gave practically no detectable ionization current.

Introduction of NO in a flow of O_2, causing their reaction between the electrodes, the pressure remaining constant, gives a very distinct electrical effect. The needle moves in a direction corresponding to a capture by the inner electrode of ions of the same sign as the external one. But after a short time the needle remains again practically stable as in pure O_2. Suppressing the flow of NO produces an electrical effect of the same magnitude but opposite sign to the first. The needle comes back to its initial position. So the curve: needle potential with respect to the time, can be divided in five parts (Fig. 5):

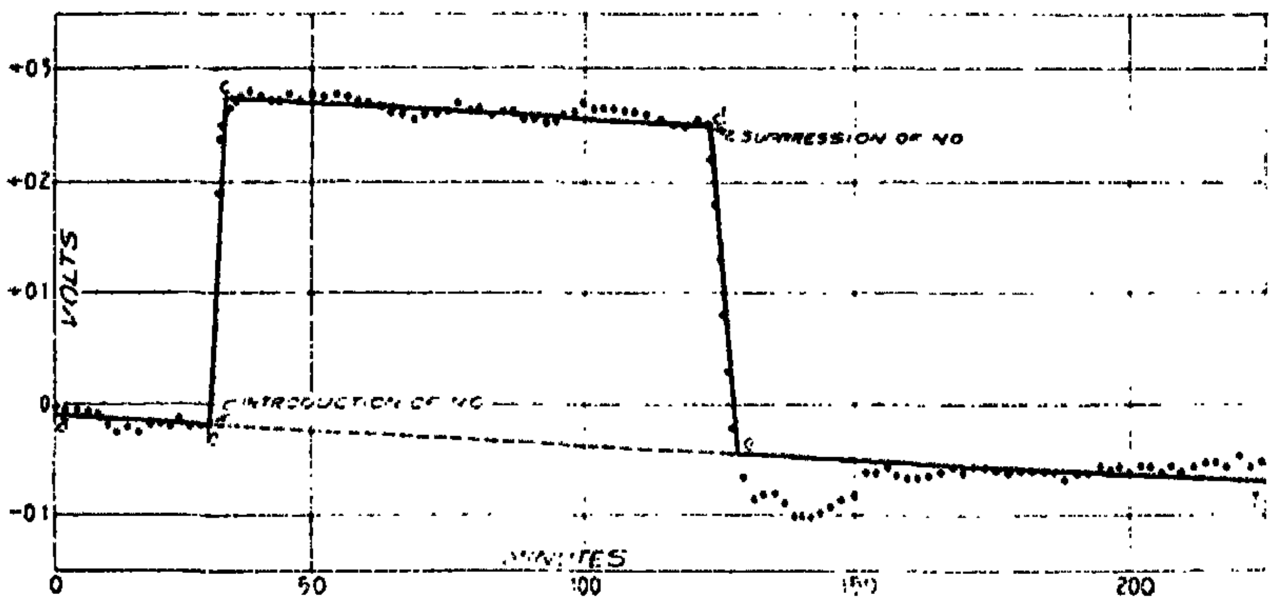

Fig 5

a-b: corresponds to a flow of pure O_2 and practically no ionization.

At b: the flow of NO is introduced, and the part b-c indicates an intense capture of charges by the inner electrode, during a short time (from a few minutes to 10 seconds). The corresponding variation of potential is approximately 0.3 v.

c-d (always with the reacting mixture) correspond to practically no more capture of charges.

At d, the flow of NO is suppressed, and d-e corresponds to the effect opposite to b-c and is also very brief.

Finally, in pure O_2, e-f, practically no ionization can be detected at all.

This curve, Fig. 5, corresponds to a positive charge of the external electrode. Using a negative charge would give a symmetrically opposite curve. Such a curve shows that the electrical effect is purely *temporary*. A permanent one would have given a part bc continuing as long as NO is flowing in the chamber, and absolutely no stop like cd, nor retrograde effect like de.

The stop at c is not due to an electrical leak because if the needle is charged to a higher voltage than c, it remains constant at this higher potential.

A second series of experiments was made with chamber II, at temperatures from 20° to 90°C; potential gradients ± 1500 v/cm and ± 1800 v/cm; flows of gases nearly 3 liters/hour. The curves were absolutely identical to those of the first series. Only the magnitude of the initial and final effect was from 0.05 to 0.09 v instead of 0.3 v. (It is interesting to note that the electrical capacity of chamber II is nearly a quarter of that of chamber I.)

A third series of experiments was carried on with chamber II; temperatures from 20° to 100°C; potential gradient from ±1500 v/cm to ±1800 v/cm; flow of NO = 3 liters/hour; *but very rapid flows of oxygen* = 40 liters/hour. No permanent effect could be observed. The initial and final effects were smaller than for the second series.

TABLE I

Chamber No. II. Pressure = 655 mm Hg. Flow O_2 = 38/42 liters per hour
Potential gradient between Electrodes = 4000 volts
Temperature = 300°C

Exp.	F_{NO}	m	i	n	n/m
52	760	$5.8.10^{18}$	2.10^{-15}	$0.1.10^{5}$	$0.2.10^{-14}$
53	1510	11.6 "	$0.7.10^{-13}$	$4.3.10^{5}$	$1.6.10^{-14}$
54	3600	27.6 "	$1.3.10^{-13}$	$7.9.10^{5}$	1.6 "
55	7500	57.5 "	1.7 "	$10.5.10^{5}$	1.9 "
56	15000	114.9 "	2.8 "	$17.4.10^{5}$	1.5 "

F_{NO} = intensity of the flow of NO
m = number of reacting molecules
i = intensity of the ionization current
n = number of charges captured per second

Experiments from 250° to 325°C.

Experiments were performed with chamber II; potential gradients from ±1600 v/cm to ±4000 v/cm; flows of NO from 1.5 to 15 liters/hour; flow of oxygen = 40 liters/hour. These experiments showed always a permanent ionization (Fig. 6). The ionization current practically zero in pure O_2 (ab) increases very strongly with the introduction into the chamber of NO which reacts with oxygen (b-d). The final effect due to the suppression of NO (d-e) is strongly diminished.

The permanent ionization, measured by the compensation method, gives currents from 2.10^{-14} to 4.10^{-13} amps. "n/m" is calculated to be of the order of 10^{-14}. Some of these results are shown in table 5, from which it is seen that increasing m 10 times increased n proportionally, but leaves n/m practically unchanged. (The results, however, were not very reproducible.)

Experiments with nitrogen peroxide at 300°.

Some experiments were performed at 300°, introducing into the chamber simultaneously O_2 and *NO_2 in equilibrium of temperature.* NO_2 is prepared by calcination of $Pb(NO_3)_2$, dried and liquefied. The flow is regulated by

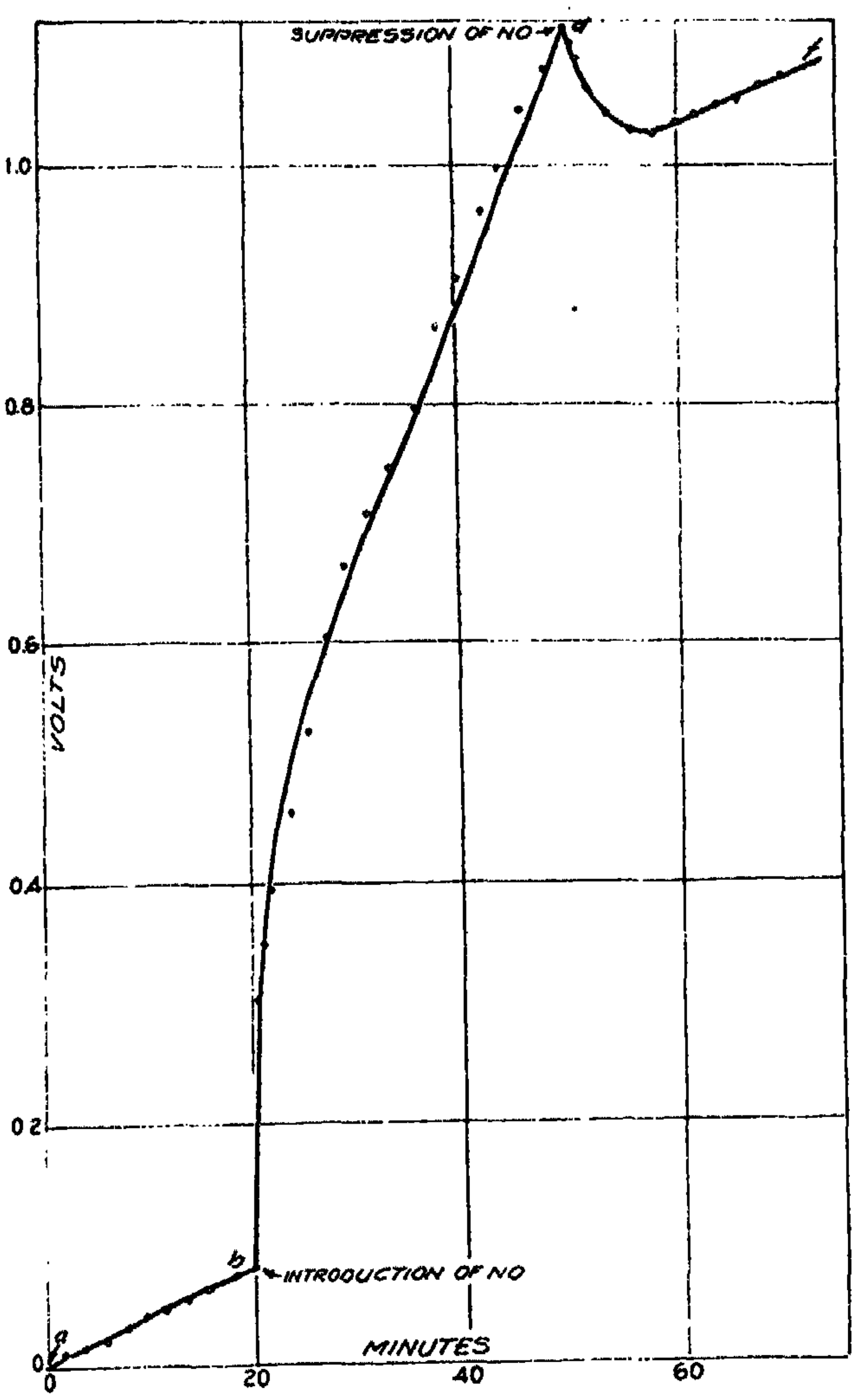

FIG. 6

the speed of evaporation so as to have the same % of NO_2 as in the previous experiments. *The results were absolutely identical to those with NO.* The form and amplitude of the curves are exactly the same.

Discussion

The results may be summarized:

a) At low temperature, in the reacting mixture $NO + O_2$, there are initial and final, but no permanent, effects.

b) At 300°, the reacting mixture $NO + O_2$ shows a permanent ionization. But the same ionization is observed in the system $2\ NO_2 \rightleftarrows 2\ NO + O_2$ in dynamical equilibrium.

Three kinds of interpretation are possible:

A first interpretation is that the reaction of $NO + O_2$ is accompanied by an ionization at low temperature as well as at high; but in the first case there is an adsorbed layer of gas on the electrodes, preventing the ions from discharging on them. Such a layer could be for instance formed on oriented dipolar molecules of NO_2. The hypothesis of such an insulating layer has been mentioned by some authors[1,2].

In order to verify this theory, experiments with fast flow of O_2 were performed. The partial pressure of NO_2 being extremely diminished, it was hoped this could diminish its adsorption, giving the possibility of a discontinuous layer and the possibility of detecting an ionization. The result was negative. Another verification consisted in introducing into the chamber at room temperature, first O_2 ionized very feebly ($i = 10^{-15}$ amp) by radioactive material, and then introducing simultaneously $O_2 + NO_2$. This introduction did not prevent the capture of ions, since the current remained the same. Therefore with the apparatus of the sensitivity employed, it was impossible to detect the existence of an insulating layer.[3]

A second interpretation is that there is no ionization in volume, but only electrical surface phenomenon. Gases in contact with metals could be ionized at relatively low temperatures, as was recently pointed out by Brewer;[4] electrical phenomena occurring in the process of *adsorption* of gases by electrodes were mentioned too by Finch and Stimson.[5] But in fact the present work did not show any evidence of such a mechanism of permanent ionization. Frequently Brewer's results could not be reproduced, for instance the ionization of 10^{-15} amp in pure O_2 at 385°C, the present apparatus being five times more sensitive than his.

A third interpretation is that only the reaction of dissociation of nitrogen peroxide, following the scheme $2\ NO_2 = 2\ NO + O_2$, is the ionizing step. In this case, the observed effect at low temperatures could be attributed to the variation of dielectric constant of the gaseous mixture between the electrodes.

There are practically no chances to prove the first hypothesis. In dynamic equilibrium we must indeed consider the two opposite reactions:

a) $2\ NO + O_2 = 2\ NO_2$ and b) $2\ NO_2 = 2\ NO + O_2$.

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[1] Bancroft: J. Phys. Chem., **29**, 20 (1925) (a review of the question).

[2] Zeleny: Phys. Rev. (2) **3**, 69 (1914); **16**, 102 (1920).

[3] It is evidently always possible to suppose that the ions formed by the reaction could be different from those produced by a radioactive substance. They could be for instance enormous clusters of mols around one ion, or they could have a very short life. Both would result in a small kinetic energy so that they could not break a gas layer not insulating for ordinary ions.

[4] Phys. Rev., (2) **26**, 633 (1925); Proc. Nat. Acad. Sci., **12**, 560 (1926); **13**, 593 (1927).

[5] G. T. Finch and J. C. Stimson: Proc. Roy. Soc., **116**, 379 (1927); **120**, 235 (1928).

At room temperatures the reaction proceeds practically only according to a). But at high temperatures the second reaction becomes very important and it is then very difficult to prove, by a direct experiment, what part a) or b) plays in the ionization.

As for the dielectric constant, some experiments were performed as follows: To a flow of O_2 in the chamber at ordinary temperatures was added a flow of N_2. The jump of the needle, corresponding to (b-c) of the curves, was practically imperceptible. (Now, the difference in dielectric constant between O_2 and N_2 is practically inappreciable.) But, if instead of N_2, HCl of high dielectric constant was introduced, an intial and final effect was observed which was practically the same as with NO or NO_2 in the same condition.

Let $K_{O_2} = 1.00055$ and $K_{NO_2} = 1.0018$ be the dielectric constants[1] of O_2 and NO_2. The variation of electrical capacity produced by replacing pure oxygen in the chamber by the mixture of O_2 and NO_2, containing x% of NO_2, will be, if *c* is the capacity in e.s.u. of the chamber in vacuo:

$$Dc = \frac{c \cdot K_{O_2}(100-x) + K_{NO_2} \cdot x}{100} - cK_{O_2} = \frac{c\,x}{100}(K_{NO_2} - K_{O_2}) \text{ e.s.u.}$$

If the external electrode be charged at v volts, and the total capacity of the electrical apparatus be C (e.s.u.), there will correspond to the previous variation of capacity a variation Dv of the potential of the needle:

$$D\,v = \frac{v}{C} \cdot c\,x \frac{(K_{NO_2} - K_{O_2}}{100} \text{ volts} \tag{5}$$

Taking for instance an experiment in which: c = 4.8 cm; C = 35.1 cm: V = 500 volts; x = 67%, we get

$$D\,V = \frac{500}{35.1} \frac{4.8 \cdot 67 \cdot 0.00125}{100} = 0.06 \text{ volts.}$$

This is precisely the order of magnitude observed. From formula (5), it is easy to see that the amplitude of the initial and final effect must be proportional to the V, to the % of NO_2 as the experiment shows.

It seems now more logical to admit the ionizing phase to be the dissociation of NO_2. Therefore, experiments are being continued to throw some light on the mechanism of the reaction of NO with O_2. No interpretation of the mechanism could be given in the present state of the subject. It would be very interesting to know if every dissociation of NO_2 is an ionizing one. In this case, owing to the small value of n/m, the ions should have a very short life.[2] Another interesting point is, if the reaction gives ionized products only when the reacting molecules of NO_2 possess, after their formation, a

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[1] From Landolt-Börnstein's Tabellen: Value corresponding at 60°C.

[2] We know nothing about the frequency and the speed of the inverse reactions occurring at equilibrium. However, the possibility of detecting an ionization at low temperature seems not very probable.

total energy above some definite value, and if they could have not yet spent this energy to activate some other reacting product. Finally it would be of use to know what kind of ions are formed.

The experiments are *continued in these directions.*

Summary

1) An electrical apparatus capable of measuring currents of 10^{-15} to 10^{-16} amps was constructed for the study of the reacting system $2\ NO + O_2 = 2\ NO_2$ and $2\ NO_2 = 2\ NO + O_2$.

2) At room temperature and at 100°C, the introduction of the reacting mixture into the ionizing chamber produced no permanent ionization. Only an initial and final effect was obtained as when taking instead of NO_2, HCl of nearly the same dielectric constant.

3) At 300°, both the reacting mixture and the mixture at equilibrium gave a permanent ionization, from 10^{-14} to 10^{-15} amps. This ionization is proportional to the potential gradient in the chamber and to the % of NO or NO_2.

4) Among the different possible interpretations, the most probable one is that the ionization is produced by the dissociation of nitrogen peroxide.

I take this opportunity to express my sincere gratitude to Professor A. Pinkus for his valuable suggestions and his kind direction during this work. This work was partially performed with the help of the "Institut International de Chimie Solvay."

Brussels University, 1926-28.
Yale University, 1929.

THE DISTRIBUTION RATIOS OF SOME ORGANIC ACIDS BETWEEN WATER AND ORGANIC LIQUIDS*

BY HOMER W. SMITH AND T. A. WHITE

Numerous investigators have called attention to an apparently close correlation between the distribution coefficients of organic substances between water and various organic liquids and the velocity with which these substances penetrate living cells. This is particularly true of the organic acids, where the penetration of definite quantity of acid can be detected by changes in the color of the intracellular pigments, artificial indicators, or by other criteria. The literature dealing with these phenomena has been recently reviewed by Jacobs,[1] Gellhorn,[2] and Taylor.[3]

One difficulty which prevents a more exact analysis of this problem is the absence of data on the true distribution ratios of the various substances used. It was long ago pointed by Nernst[4] that the distribution law would apply only to such molecular species as were common to both solvents. If the solute is associated in one solvent (as is the case with most organic acids in organic solvents) or dissociated in the other (as happens with all acids in water) the gross distribution ratio tends to change with changing concentration of solute, and the division of the solute between the two solvents is only indirectly related to the distribution ratio of the simple molecules of solute. This latter value can in such a case be determined only when the degree of association in the organic layer or the degree of dissociation in the water are known.

The general theory of the distribution of a substance between two immiscible liquids has been reviewed by Hill,[5] and only certain aspects of this theory need be mentioned here. If it is assumed that association in the organic layer proceeds to the formation of dimeric molecules, and that the equilibrium between these dimeric molecules and the simple molecules present is governed by the mass law, it is possible by simultaneous equations derived from the mass law and by knowledge of the degree of dissociation in water to calculate from the gross distribution at two concentrations both the distribution ratio for the simple molecules and the association constant governing the process of association in the organic layer. The success of this method depends on the assumption, which is broadly established for the organic acids, that the solute is not significantly dissociated in organic liquids nor polymerized in water.

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[*] From the Department of Physiology and the Department of Chemistry, University of Virginia.

[1] "General Cytology" (1924).

[2] "Das Permeäbilitatsproblem" (1929).

[3] J. Gen. Physiol., 11, 207 (1927-28).

[4] Z. physik. Chem., 8, 110 (1891).

[5] "Treatise on Physical Chemistry" (1925).

Equations of this type were derived by Hendrixson[1] and applied to the distribution of benzoic acid and salicyclic acid between water and benzene and between water and chloroform.

With a view to adding to our knowledge of the behavior of the organic acids in heterogeneous systems, we have determined the distribution ratios and association constants of a number of these substances in the systems water:toluene, water:benzene and water:chloroform. It is thought that these data may also be of some interest to students of molecular physics.

Methods

Glass-stoppered bottles containing mixtures of water, the organic solvent and solute were suspended in a water bath maintained at 25°C. ±0.5°. Mixing was effected by regularly removing the bottles and shaking. Samples were removed by pipetting out known amounts from each layer, after which equivalent amounts of each solvent were replaced and the bottle again brought to temperature and shaken. The samples were titrated in some cases with NaOH, in others with dilute $Ba(OH)_2$ protected from CO_2. Titrations were carried out with phenol red and phenolphthalein as indicators. In some instances the concentration in the organic layer was determined by difference, but usually the organic liquid was titrated directly after the addition of a little water.

The solvents were redistilled before use, the first and final fraction being discarded. Some of the aromatic acids were purified by recrystallization, but the aliphatic acids were used without attempt at repurification. All the acids were highest grade, C.P. products.

The calculation of the distribution ratio, P, and of the association constant, K, were made as follows:

C_1 = concentration in aqueous layer in millimols per liter.
C_2 = concentration in organic layer in millimols per liter.
α = degree of dissociation of single molecules into ions in aqueous layer.
$P = \dfrac{\text{concentration of single molecules in organic layer}}{\text{concentration of single molecules in aqueous layer}}$.
K = association constant in organic layer of double into single molecules.

Assuming that the process of association in the organic layer follows the mass law, then for any two concentrations

$$K = \frac{[PC_1(1-\alpha)]^2}{C_2 - PC_1(1-\alpha)} = \frac{[PC_1'(1-\alpha')]^2}{C_2' - PC_1'(1-\alpha')} \qquad (1)$$

If we write

$$N = C_1(1-\alpha) \qquad (2)$$

$$n = C_1'(1-\alpha') \qquad (3)$$

Where $1-\alpha$ is calculated from Ostwald's dilution law using the dissociation constants given by Scudder[2] for the substances under investigation, and solve equation (1) for P, the following expression is obtained

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[1] Z. anorg. Chem., 12, 73 (1897).

[2] "The Electrical Conductivity and Ionization Constants of Organic Compounds" (1914).

$$P = \frac{C_2 n^2 - C_2' N^2}{(n - N) n N} \tag{4}$$

The association constant, K, in the organic layer is obtained by substituting determined values of P in equation (1).

It is apparent from (4) that C_2/N^2 should bear a linear relation to $1/N$, the slope of the curve being equal to P. By plotting the experimentally determined values of C_2/N^2 and $1/N$, it is possible to eliminate those values of C_2/N^2 which are aberrant, and to choose a value of C_2/N^2 consonant with the majority to serve as a basic term of the series from which to calculate the successive values of P. In view of the fact that in many instances the higher terms of C_1 and C_2 approach concentrated solutions in which the simple partition law is not valid, this preliminary graphical treatment is a necessary precaution, otherwise a whole series of relatively accurate values may be thrown into error by the unadvised choice of a basal aberrant term.[1]

Results

The results of our determinations are collected in the following tables. Tables I, II, and III deal respectively with the water:toluene, water:benzene, and the water:chloroform systems. C_1, C_2, P, and K have the significance already given to them.

TABLE I

			Toluene	
	C_1	C_2	P	$K \times 10^3$
Acetylsalicyclic	15.80	10.10	0.320	3.33
Acid	14.00	8.18	0.330	3.40
	11.22	5.81	0.313	3.26
	10.40	5.12	0.319	3.32
	9.37	4.36	0.318	3.30
	8.45	3.70	0.325	3.32
	7.52	3.10		3.33
Mean			0.320	3.32
Anisic	1.72	9.50	3.24	6.2
Acid	1.58	8.18	3.38	6.5
	1.45	7.00	3.57	7.0
	1.32	6.07	3.70	7.1
	1.19	5.28	3.55	6.8
	1.056	4.49	3.40	6.0
	0.924	3.70		6.9
Mean			3.46	6.6

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[1] We are indebted to Carlotta Greene Smith for assistance in a large part of this work.

TABLE I (Continued)

	Toluene			
	C_1	C_2	P	K × 10^3
Benzilic	3.85	5.50	1.96	35.2
Acid	3.74	5.28	1.98	36.5
	3.63	5.00	2.01	40.5
	3.40	4.62	1.99	37.6
	3.23	4.36	2.00	38.1
	2.84	3.63	2.02	38.4
	2.38	2.90		37.5
Mean			1.99	37.7
Benzoic	13.5	162.0	2.23	6.33
Acid	12.0	128.4	2.24	6.26
	10.8	105.6	2.29	6.31
	10.5	100.6	2.26	6.27
	9.6	82.5	2.30	6.49
	8.1	62.4	2.35	6.32
	7.2	50.4	2.40	6.38
	5.7	33.6		6.29
Mean			2.29	6.33
Bromoacetic	92.90	2.25	0.0262	
Acid	63.15	1.43	0.0285	
	42.85	0.970	0.0261	about 50,000
	38.49	0.805	0.0268	
	30.90	0.660	0.0264	
	24.43	0.535	0.0250	
	17.95	0.358	0.0260	
	13.56	0.260		
Mean			0.0265	
α-Bromo-n-butyric	42.15	48.20	0.440	7.87
Acid	31.90	29.20	0.443	7.98
	23.86	17.99	0.434	7.67
	19.64	13.03	0.435	7.77
	17.37	10.58	0.443	7.73
	14.69	8.00	0.452	8.28
	12.90	6.58	0.451	8.10
	11.38	5.41	0.462	8.20
	8.87	3.77		7.89
Mean			0.443	7.93

TABLE I (Continued)

	Toluene			
	C_1	C_2	P	$K \times 10^3$
α-Bromopropionic Acid	67.60	14.25	0.137	10.6
	49.09	8.71	0.138	11.6
	40.12	6.90	0.136	9.7
	31.00	4.55	0.140	12.1
	25.81	3.60	0.139	11.6
	19.56	2.55	0.136	10.6
	14.96	1.80	0.135	10.7
	11.95	1.37		9.4
Mean			0.137	10.8
β-Bromopropionic Acid	97.65	23.55	0.1066	7.58
	67.48	12.87	0.1069	8.02
	52.01	8.38	0.1091	(9.17)
	33.60	4.92	0.1054	7.52
	23.02	2.97	0.1065	7.87
	19.57	2.43	0.1049	7.30
	15.89	1.79	0.1060	7.86
	11.35	1.26		7.94
Mean			0.1065	7.73
α-Bromo-n-valeric Acid	14.30	54.80	1.79	11.4
	11.95	39.95	1.76	11.1
	9.80	27.60	1.79	11.4
	8.82	22.58	1.88	12.2
	8.01	19.28	1.84	11.6
	7.58	17.31	1.81	11.8
	6.82	14.15	1.83	12.6
	6.05	11.46	1.82	13.1
	5.45	10.16	1.84	11.7
	4.70	7.90		11.8
Mean			1.82	11.9
Iso-Butyric Acid	207.2	484.8	0.1366	1.70
	160.9	300.1	0.1355	1.69
	94.40	108.8	0.1344	1.66
	53.08	36.62	0.1363	1.69
	38.80	20.82	0.1362	1.69
	22.78	8.50	0.1330	1.65
	17.44	5.39	0.1378	1.70
	8.18	1.73		1.68
Mean			0.1357	1.68

TABLE I (Continued)

Toluene

		C_1	C_2	P	$K \times 10^2$
n-Butyric Acid		234.1	471.9	0.154	2.82
		179.4	290.6	0.153	2.73
		124.9	151.9	0.151	2.61
		67.75	51.15	0.150	2.53
		41.43	21.17	0.149	2.51
		25.41	9.40	0.149	2.48
		16.51	4.74	0.149	2.53
		7.81	1.62	0.154	2.69
		4.57	0.813		2.63
	Mean			0.151	2.61
n-Caproic Acid		6.07	102.36	3.66	4.82
		4.94	70.63	3.59	4.77
		4.91	71.35	3.33	4.71
		4.12	52.38	3.14	4.59
		3.85	45.31	3.57	4.73
		2.81	26.37	3.45	4.70
		2.63	23.77	3.39	4.70
		2.36	19.56		4.71
	Mean			3.45	4.72
m-Chlorobenzoic Acid		1.52	25.1	13.3	21.1
		1.39	22.2	13.5	21.3
		1.19	16.9	13.2	21.1
		1.07	14.1	13.5	21.2
		0.99	12.8	12.8	21.1
		0.924	11.48		21.2
	Mean			13.3	21.2
o-Chlorobenzoic Acid		7.92	31.9	1.74	3.71
		6.86	23.8	1.79	3.73
		5.81	17.2	1.75	3.72
		5.28	14.3	1.77	3.71
		4.62	11.0	1.71	3.71
		4.49	10.56	1.64	3.68
		4.22	9.31		3.69
	Mean			1.72	3.71
p-Chlorobenzoic Acid		0.660	4.40	17.	
		0.585	3.77	19.	
		0.520	3.64	20.	
		0.455	3.51	19.	
		0.416	3.33		
	Mean			19.	

TABLE I (Continued)

	Toluene			
	C_1	C_2	P	K × 10^3
β-Chloropropionic Acid	83.82	9.34	0.0582	4.99
	55.95	5.04	0.0587	5.30
	42.63	3.48	0.0587	5.25
	26.19	1.85	0.0587	5.34
	23.03	1.57	0.0592	5.55
	20.18	1.34	0.0590	5.44
	17.14	1.11	0.0584	5.27
	11.47	0.69		5.25
Mean			0.0587	5.28
Cinnamic Acid	2.64	139.7	38.8	19.3
	2.44	121.5	39.7	20.6
	2.27	105.0	42.8	24.6
	1.75	79.0	37.9	19.4
	1.26	50.6		20.8
Mean			39.9	20.9
α-Crotonic Acid	126.10	117.70	0.0978	1.328
	95.50	74.60	0.0963	1.339
	65.20	34.40	0.0935	1.318
	47.40	19.22	0.0941	1.322
	32.28	9.77	0.0947	1.329
	19.50	4.22		1.333
Mean			0.0953	1.328
Iodoacetic Acid	73.50	6.175	0.0604	7.5
	50.20	3.665	0.0602	7.4
	39.71	2.685	0.0603	7.5
	36.25	2.350	0.0610	8.2
	33.33	2.095	0.0616	8.6
	30.49	1.900	0.0606	7.8
	28.42	1.750	0.0604	7.6
	25.95	1.575	0.0595	7.2
	20.61	1.180	0.0595	7.4
	15.80	0.850		7.7
Mean			0.0604	7.7
β-Iodopropionic Acid	51.36	42.9	0.235	4.26
	37.96	25.42	0.235	4.26
	28.93	16.12	0.235	4.27
	21.42	9.92	0.235	4.25
	15.45	5.92	0.238	(4.41)
	7.78	2.26	0.242	(4.38)
	6.44	1.77		4.26
Mean			0.235	4.26

TABLE I (Continued)

		Toluene		
	C_1	C_2	P	$K \times 10^3$
Methylanthranilic Acid	2.20	6.82	3.95	
	1.85	5.80	4.03	
	1.58	5.02	4.08	
	1.32	4.36	4.03	
	1.12	3.70	4.29	
	0.924	3.17		
Mean			4.08	
o-Methoxybenzoic Acid	17.8	62.0	2.83	134.
	15.6	53.7	2.73	121.
	14.1	46.0	2.86	142.
	12.5	39.8	2.78	132.
	11.0	34.5	2.72	123.
	9.68	29.7	2.74	117.
	7.70	22.2		128.
Mean			2.78	128.
o-Nitrobenzoic Acid	13.0	2.22	0.455	
	9.90	1.65	0.479	
	8.69	1.45	0.468	
	7.48	1.25	0.451	
	6.60	1.06	0.467	
	5.72	0.898		
Mean			0.463	
m-Nitrobenzoic Acid	9.37	23.1	1.25	6.57
	8.51	19.6	1.23	6.49
	7.69	16.7	1.17	6.34
	6.37	12.1	1.20	6.45
	5.87	10.56	1.19	6.45
	5.28	8.80	1.27	6.52
	4.75	7.48		6.47
Mean			1.22	6.47
p-Nitrobenzoic Acid	1.12	0.980	3.2	
	0.784	0.812	3.2	
	0.588	0.630	3.2	
	0.504	0.530	3.3	
	0.420	0.448	3.1	
	0.336	0.336		
Mean			3.2	

TABLE I (Continued)

Toluene

		C_1	C_2	P	$K \times 10^3$
Phenylacetic		19.90	70.80	0.734	3.48
Acid		16.67	50.89	0.750	3.52
		13.49	34.35	0.763	3.58
		11.39	25.91	0.734	3.49
		5.09	3.81		
	Mean			0.745	3.52
Propionic		477.1	132.9	0.0469	4.22
Acid		311.0	61.10	0.0470	4.23
		211.0	35.00	0.0452	3.58
		127.1	14.90	0.0452	3.60
		79.48	7.05	0.0455	3.69
		51.21	3.82	0.0445	3.48
		31.46	1.99	0.0449	3.61
		18.89	1.02		3.86
	Mean			0.0456	3.78
Salicylic		12.1	30.8	1.99	28.1
Acid		10.9	25.1	2.08	31.4
		9.24	19.9	2.05	29.9
		7.70	15.4	2.00	29.7
		6.82	12.4	2.19	32.3
		6.60	11.9	1.95	30.9
		5.72	9.79	2.08	29.8
		5.50	9.24		30.2
	Mean			2.05	30.3
o-Toluic		3.56	99.0	12.6	22.3
Acid		3.30	87.0	12.3	22.4
		3.04	74.8	13.1	22.5
		2.77	64.0	12.3	22.1
		2.57	56.5		22.1
	Mean			12.6	22.3
p-Toluic		2.11	52.8	4.56	1.73
Acid		1.98	46.6	4.55	1.74
		1.85	40.5	4.88	1.75
		1.72	35.5	4.95	1.75
		1.59	30.1	5.13	1.75
		1.45	25.5		1.73
	Mean			4.8	1.74

TABLE I (Continued)

Toluene

	C_1	C_2	P	$K \times 10^3$
Iso-Valeric Acid	24.18	60.67	0.455	2.18
	21.00	46.20	0.466	2.23
	17.79	34.94	0.450	2.17
	15.16	26.59	0.437	2.12
	13.07	20.61	0.426	2.10
	10.86	14.82	0.433	2.12
	8.74	10.16	0.445	2.15
	6.995	6.885	0.447	2.24
	5.552	4.92		2.11
Mean			0.445	2.17
n-Valeric Acid	28.89	138.5	0.646	26.2
	21.60	80.75	0.646	25.9
	15.46	45.43	0.636	24.7
	11.25	25.95	0.634	24.4
	7.11	11.92	0.630	23.8
	4.91	6.68	0.617	22.7
	1.95	1.68	0.600	22.7
	1.64	1.30	0.631	23.8
	1.32	0.979		24.0
Mean			0.630	24.3

TABLE II

Benzene

	C_1	C_2	P	$K \times 10^3$
Bromoacetic Acid	91.85	2.78	0.0368	
	62.25	1.88	0.0356	
	42.41	1.19	0.0362	
	37.99	1.06	0.0363	
	30.58	0.82	0.0365	
	24.21	0.65	0.0373	
	17.76	0.48	0.0349	
	13.39	0.35		
Mean			0.0362	
α-Bromo-n-butyric Acid	37.78	52.57	0.702	17.1
	28.38	32.72	0.695	17.0
	21.34	20.51	0.704	17.4
	17.44	15.23	0.693	16.7
	15.47	12.48	0.707	17.7
	13.07	9.62	0.719	18.4
	11.53	7.95	0.718	19.0
	10.10	6.69	0.714	17.8
	7.86	4.71		17.9
Mean			0.708	17.7

TABLE II (Continued)

	Benzene			
	C_1	C_2	P	$K \times 10^2$
α-Bromopropionic Acid	63.29	18.56	0.212	20.4
	46.00	11.80	0.212	20.4
	37.52	9.10	0.212	20.1
	29.17	6.38	0.212	20.4
	24.34	5.07	0.211	20.1
	18.49	3.52	0.213	(21.0)
	14.12	2.54	0.211	(19.5)
	11.32	1.92		20.1
Mean			0.212	20.3
β-Bromopropionic Acid	91.70	31.50	0.141	8.1
	62.80	17.55	0.139	7.9
	48.40	11.99	0.138	7.7
	32.01	6.51	0.142	8.3
	22.03	3.96	0.137	7.8
	18.81	3.19	0.141	8.1
	15.20	2.48		7.5
Mean			0.140	8.0
α-Bromo-n-valeric Acid	12.85	56.25	2.31	13.9
	10.71	41.19	2.27	14.7
	8.79	28.62	2.32	17.6
	7.83	23.57	2.30	15.0
	7.18	20.12	2.35	15.3
	6.77	18.13	2.27	15.4
	6.01	14.96	2.37	15.3
	5.34	12.38	2.28	15.0
	4.75	10.42		14.2
Mean			2.32	15.2
Iso-Butyric Acid	190.6	501.4	0.191	2.75
	147.0	313.0	0.187	2.70
	87.7	115.6	0.189	2.71
	49.3	40.4	0.188	2.69
	36.4	23.2	0.191	2.75
	21.5	9.78	0.191	2.70
	16.4	6.39	0.188	2.71
	9.95	3.02	0.191	2.72
	7.74	2.13		2.69
Mean			0.189	2.70

TABLE II (Continued)

Benzene

	C_1	C_2	P	$K \times 10^5$
n-Butyric	216.3	489.7	0.225	5.22
Acid	166.1	303.9	0.224	5.07
	117.1	159.7	0.224	5.02
	63.80	54.10	0.223	4.95
	39.21	23.40	0.224	5.00
	24.03	10.78	0.224	4.98
	15.65	5.60	0.225	5.16
	7.35	2.08	0.225	5.09
	4.40	1.10		4.91
Mean			0.224	5.02
n-Caproic	5.68	103.10	4.27	6.65
Acid	3.88	52.87	4.29	6.64
	3.60	45.80	4.24	6.64
	2.63	26.75	4.14	6.61
	2.47	24.08	4.42	6.67
	2.19	19.89		6.64
Mean			4.27	6.64
Iso-Caproic	9.22	180.0	3.6	6.06
Acid	8.07	142.0	3.5	5.98
	7.58	125.0	3.8	6.02
	6.85	103.0	4.1	6.06
	6.15	87.4	2.2	5.58
	5.64	74.2	2.8	5.89
	4.98	58.9		5.95
Mean			3.4	5.97
β-Chloropropionic	78.82	11.59	0.0872	8.9
Acid	52.82	6.61	0.0872	9.0
	40.41	4.59	0.0876	9.4
	28.30	2.96	0.0879	8.8
	24.89	2.50	0.0871	9.4
	21.90	2.13	0.0882	9.6
	19.20	1.83	0.0874	9.2
	16.32	1.52	0.0876	9.2
	10.94	0.956		9.0
Mean			0.0873	9.2

TABLE II (Continued)

		Benzene		
	C_1	C_2	P	$K \times 10^3$
α-Crotonic Acid	118.2	125.6	0.121	1.81
	93.7	80.4	0.122	1.84
	62.15	37.45	0.123	1.85
	45.20	21.42	0.121	1.82
	31.00	11.05	0.123	1.85
	18.74	4.85	0.119	1.85
	11.06	2.20	0.122	1.84
	9.69	1.83		1.82
Mean			0.122	1.83
Iodoacetic Acid	70.70	7.58	0.0822	12.6
	48.40	4.57	0.0822	12.7
	38.40	3.34	0.0830	14.1
	35.30	3.00	0.0832	14.2
	32.21	2.66	0.0841	15.2
	29.50	2.40	0.0839	15.0
	27.48	2.22	0.0827	13.7
	25.31	1.97	0.0853	16.5
	19.96	1.51	0.0839	14.4
	15.43	1.11		14.1
Mean			0.0831	14.2
β-Iodopropionic Acid	46.60	47.75	0.322	6.02
	34.46	28.92	0.319	5.90
	26.35	18.70	0.318	5.84
	19.56	11.78	0.315	5.72
	14.20	7.17	0.318	5.86
	9.87	4.24	0.332	6.20
	7.20	2.78	0.315	5.80
	5.98	2.17		5.88
Mean			0.319	5.90
Phenylacetic Acid	16.26	74.54	1.00	3.98
	13.64	59.92	1.00	3.98
	11.02	36.82	1.02	3.99
	9.35	27.95	0.96	3.90
	7.32	18.12	1.00	3.96
	5.80	12.33	0.98	3.94
	5.14	9.98	1.09	4.03
	4.30	7.61		3.93
Mean			1.00	3.95

TABLE II (Continued)

Benzene

		C_1	C_2	P	$K \times 10^3$
Propionic Acid		454.0	156.0	0.0629	5.78
		297.9	74.2	0.0596	5.67
		206.2	39.8	0.0606	5.58
		124.1	17.9	0.0598	5.24
		78.0	8.58	0.0604	5.48
		50.3	4.72	0.0590	5.16
		31.0	2.45	0.0604	5.49
		18.6	1.31		5.54
	Mean			0.0604	5.49
Iso-Valeric Acid		22.31	62.54	0.590	3.21
		19.15	48.05	0.575	3.14
		16.44	32.29	0.582	3.17
		14.04	27.71	0.575	3.15
		12.14	21.54	0.572	3.14
		8.08	10.82	0.592	3.18
		6.41	7.47	0.612	3.20
		5.10	5.26		3.20
	Mean			0.582	3.17
n-Valeric Acid		26.61	140.79	0.828	3.72
		19.81	82.54	0.823	3.66
		14.40	46.49	0.823	3.64
		10.41	26.79	0.815	3.55
		6.55	12.47	0.808	3.82
		4.54	7.06	0.797	3.37
		1.77	1.79	0.802	3.53
		1.50	1.44		3.54
	Mean			0.814	3.60

TABLE III

Chloroform

		C_1	C_2	P	$K \times 10^3$
Acetylsalicyclic Acid		19.8	181.0	1.77	6.62
		16.1	120.0	1.87	6.66
		14.8	102.3	1.78	6.66
		13.7	88.2	1.78	6.69
		12.7	76.4	1.88	6.72
		9.4	44.0		6.66
	Mean			1.81	6.67

TABLE III (Continued)

Chloroform

	C_1	C_2	P	$K \times 10^2$
Anisic Acid	1.78	47.8	29.4	1500.
	1.58	41.8	29.8	2100.
	1.39	36.1	30.7	3600.
	1.19	30.6	29.9	2300.
	1.06	26.8	30.8	4700.
	0.924	23.3		1300.
Mean			29.9	
Anthranilic Acid	46.98	19.96	0.0780	0.772
	32.50	10.38	0.0765	0.762
	27.35	7.66	0.0760	0.762
	20.92	4.79	0.0777	0.772
	16.07	3.06	0.0827	0.756
	11.26	1.76		0.769
Mean			0.077	0.767
Benzilic Acid	2.51	14.5	11.8	
	2.24	12.8	11.7	
	1.98	11.4	11.4	
	1.78	9.50	11.8	
	1.39	6.74	13.0	
	1.25	6.07	12.4	
	1.12	5.28		
Mean			12.0	
Benzoic Acid	6.27	84.5	4.35	12.8
	4.95	55.9	5.18	12.9
	4.49	47.5	4.90	12.7
	4.09	41.4	3.65	12.4
	3.76	35.4		12.8
Mean			4.8	12.7
o-Bromobenzoic Acid	4.89	56.7	8.14	16.1
	4.55	49.3	8.20	16.1
	4.22	42.2	7.64	15.4
	3.90	36.5	8.14	15.9
	3.43	28.2	8.48	16.1
	2.90	20.5		16.0
Mean			8.14	16.0
m-Bromobenzoic Acid	0.53	24.4	111.	
	0.46	22.7	109.	
	0.42	18.7	120.	

TABLE III (Continued)

Chloroform

	C_1	C_2	P	$K \times 10^5$
	0.35	16.5	119.	
	0.28	13.4		
Mean			115.	
α-Bromo-n-butyric Acid	26.89	51.01	0.984	15.8
	24.28	43.52	0.971	15.0
	21.64	36.21	0.963	14.8
	19.00	29.14	0.959	14.6
	17.06	24.04	0.971	15.0
	15.53	20.69	0.968	14.9
	13.87	17.50	0.947	14.4
	11.99	13.91	0.974	15.0
	9.52	9.57	0.975	15.1
	7.46	6.67		14.9
Mean			0.972	14.9
α-Bromopropionic Acid	48.10	18.05	0.315	3600.
	42.48	15.18	0.315	3600.
	39.13	13.87	0.316	3300.
	35.39	11.91	0.315	3600.
	31.38	9.92	0.320	4200.
	27.81	8.49	0.321	4300.
	25.04	7.61	0.315	3700.
	21.22	6.08	0.321	4200.
	19.29	5.60	0.320	(5400.)
	16.06	4.41	0.325	4200.
	12.22	3.11		3900.
Mean			0.318	3900.
β-Bromopropionic Acid	48.10	18.45	0.246	17.4
	28.18	8.62	0.247	19.6
	21.30	6.33	0.246	16.1
	16.17	4.56	0.245	16.5
	8.03	1.85	0.253	18.5
	4.62	1.08	0.228	
	2.97	0.63		
Mean			0.244	17.6

TABLE III (Continued)

Chloroform

		C_1	C_2	P	$K \times 10^3$
Iso-Butyric Acid		112.80	495.2	0.556	8.91
		93.80	354.1	0.552	8.83
		76.90	244.3	0.554	8.86
		63.15	172.1	0.557	8.74
		49.15	109.9	0.567	8.74
		41.01	79.69	0.549	8.78
		34.30	57.30	0.557	9.08
		33.82	54.98	0.560	9.31
		26.23	36.80	0.557	9.06
		20.31	25.89	0.544	8.15
		18.38	20.42	0.556	9.47
		14.54	14.36	0.559	9.26
		11.11	9.59	0.568	(9.84)
		6.08	4.26	0.575	(10.05)
		3.33	1.98		9.10
				0.558	9.08
n-Butyric Acid		126.0	471.0	0.529	10.8
		96.65	298.2	0.537	10.4
		81.60	232.4	0.534	9.6
		58.98	126.9	0.506	9.8
		46.70	85.20	0.524	9.7
		36.00	54.58	0.522	9.8
		35.55	55.05	0.522	9.3
		28.32	38.08	0.520	9.2
		22.89	25.46	0.525	10.3
		22.00	25.00	0.522	9.4
		14.35	12.58	0.524	10.3
		5.72	3.48	0.539	(13.8)
		3.67	2.13	0.522	10.9
		1.78	0.924		(11.2)
	Mean			0.531	10.1
n-Caproic Acid		4.40	172.5	[illegible].46	17.3
		3.98	146.5	11.26	17.0
		3.08	94.4	11.15	16.9
		2.224	54.5	11.30	(19.2)
		1.714	35.8	11.20	17.0
		1.383	25.6	10.96	16.8
		1.020	16.25		17.0
	Mean			11.22	17.0

TABLE III (Continued)

	Chloroform			
	C_1	C_2	P	K × 10^8
Iso-Caproic	3.51	92.98	(8.05)	10.0
Acid	2.31	47.18	(8.00)	9.5
	1.63	27.08	(7.96)	9.1
	1.14	15.30	7.90	8.8
	0.75	8.13	7.90	9.0
	0.41	3.58	7.90	9.1
	0.21	1.48		8.6
Mean			7.90	9.2
m-Chlorobenzoic	0.70	17.5	84.	
Acid	0.56	15.1	87.	
	0.42	13.1	89.	
	0.35	11.4	91.	
	0.28	9.4		
Mean			88.	
o-Chlorobenzoic	5.02	36.5	8.55	68.
Acid	4.49	31.2	8.34	61.
	4.03	26.4	8.20	73.
	3.57	20.7	8.86	75.
	3.17	17.6	8.55	67.
	2.90	15.2	8.93	74.
	2.64	13.2	8.86	71.
	2.31	10.8		68.
Mean			8.62	72.
p-Chlorobenzoic	0.66	8.1	50.	
Acid	0.49	7.8	51.	
	0.364	6.7	54.	
	0.28	5.8	54.	
	0.25	5.3	56.	
	0.238	5.15	54.	
	0.21	4.6		
Mean			53.	
β-Chloropropionic	82.42	19.58	0.1375	13.6
Acid	54.83	11.20	0.1365	12.9
	41.80	7.78	0.1310	12.8
	29.20	4.80	0.1383	13.9
	25.78	4.10	0.1390	14.2
	22.62	3.54	0.1375	13.2
	19.72	3.08	0.1320	11.3
	16.77	2.50	0.1343	12.3
	11.23	1.56		12.9
Mean			0.1365	13.0

TABLE III (Continued)

		Chloroform			
		C_1	C_2	P	$K \times 10^5$
Cinnamic Acid		1.32	136.4	96.	190.
		1.12	119.5	75.	140.
		0.98	92.1	95.	170.
		0.84	78.8	60.	140.
		0.77	68.4		150.
	Mean			82.	160.
α-Crotonic Acid		34.32	40.15	0.315	3.74
		27.93	27.94	0.317	3.75
		23.08	20.68	0.315	3.65
		17.25	12.58	0.311	3.70
		12.39	7.43	(0.328)	3.79
		9.02	4.66		3.71
	Mean			0.314	3.72
Iodoacetic Acid		64.65	12.20	0.1582	27.3
		50.85	8.95	0.1600	30.9
		41.90	7.08	0.1589	28.5
		38.31	6.21	0.1605	32.7
		32.13	4.96	0.1595	36.2
		27.88	4.30	0.1585	28.2
		23.50	3.45	0.1610	33.0
		20.80	3.01	0.1603	30.0
		16.55	2.30	0.1590	30.3
		13.88	1.87		29.7
	Mean		.	0.1595	30.7
β-Iodopropionic Acid		30.30	35.75	0.554	12.9
		17.99	16.50	0.554	11.9
		10.08	7.27	0.553	12.8
		6.05	3.66	0.554	(16.2)
		3.77	2.08	0.553	13.2
		2.21	0.98	0.551	
		1.27	0.56	0.555	
		0.697	0.274		
	Mean			0.554	12.8
Mandelic Acid		69.5	3.17	0.0585	
		60.5	2.90	0.0580	
		52.2	2.44	0.0590	
		45.8	2.11	0.0601	
		39.6	1.85	0.0606	
		34.8	1.65	0.0604	
		21.8	1.06		
	Mean			0.0594	

TABLE III (Continued)

	Chloroform			
	C_1	C_2	P	$K \times 10^3$
Methylanthranilic Acid	1.58	25.7	8.0	12.6
	1.45	21.8	8.9	13.4
	1.32	19.1	8.8	13.3
	1.19	16.2	9.3	13.6
	1.08	14.3	7.8	12.9
	0.99	12.5		13.3
Mean			8.5	13.2
o-Methoxybenzoic Acid	5.48	187.0	47.	
	4.75	169.0	47.	
	4.16	152.0	46.	
	3.70	132.5	48.	
	3.30	115.0	51.	
	2.44	88.6		
Mean			48.	
o-Nitrobenzoic Acid	11.95	6.34	1.03	
	10.56	5.28	1.04	
	9.44	4.36	1.06	
	8.32	3.57	1.10	
	7.26	2.97	1.10	
	6.40	2.51	1.12	
	5.61	2.11	(1.16)	
	5.08	1.85		
Mean			1.06	
m-Nitrobenzoic Acid	7.79	61.4	3.13	9.04
	7.13	52.3	3.12	8.96
	6.07	39.6	2.87	8.69
	5.68	34.5	3.10	8.98
	5.15	29.0	3.01	8.96
	4.69	24.2	3.26	9.12
	3.70	16.2		9.43
Mean			3.08	9.03
p-Nitrobenzoic Acid	1.45	4.84	7.5	
	1.25	4.09	7.6	
	1.06	3.43	7.8	
	0.924	2.97	8.1	
	0.84	2.64	8.7	
	0.70	2.24		
Mean			7.9	

TABLE III (Continued)

Chloroform

		C_1	C_2	P	$K \times 10^3$
Phenylacetic Acid		10.10	108.9	2.94	(10.4)
		7.96	73.9	2.87	8.9
		5.72	41.2	2.87	9.1
		4.83	30.5	2.97	9.3
		3.89	21.3	2.92	9.4
		3.14	14.9	2.98	9.8
		2.37	9.94	2.87	9.2
		1.94	7.35	3.00	9.5
		1.48	4.995		9.5
	Mean			2.94	9.3
Propionic Acid		415.0	335.0	0.160	15.2
		342.7	245.8	0.161	15.5
		258.0	150.0	0.161	15.4
		200.5	101.3	0.158	14.7
		129.8	49.1	0.158	14.8
		94.8	29.7	0.161	15.2
		64.3	17.5	(0.151)	16.3
		51.5	12.7	0.160	15.4
		33.05	6.95		15.1
	Mean			0.160	15.3
Salicylic Acid		5.68	22.4	2.96	13.7
		5.28	19.6	3.00	13.4
		4.89	16.9	3.10	13.3
		4.49	14.6	3.09	13.3
		4.10	12.3	3.54	13.9
		3.70	10.55		11.8
	Mean			3.13	13.2
o-Toluic Acid		4.49	310.0	5.75	1.64
		4.09	279.0	5.56	1.38
		3.70	233.0	5.88	1.44
		3.30	192.0	6.06	1.37
		2.90	170.0	5.89	1.16
		2.57	147.0	5.26	(1.02)
		2.11	112.3		(0.88)
	Mean			5.72	1.38
p-Toluic Acid		1.32	100.8	65.0	198.
		1.19	87.1	64.6	182.
		0.98	64.1	(71.4)	218.
		0.84	54.7	64.6	180.
		0.70	41.8		202.
	Mean			64.7	196.

TABLE III (Continued)

Chloroform

		C_1	C_2	P	$K \times 10^3$
Iso-Valeric Acid		15.38	91.42	1.58	7.79
		12.13	61.88	1.56	7.49
		9.89	42.31	1.58	7.69
		7.71	27.69	1.59	7.98
		5.96	19.64	1.53	7.09
		4.03	10.59	1.54	7.20
		2.76	6.27	1.49	6.92
		1.47	2.47		
	Mean			1.55	7.6
n-Valeric Acid		10.40	69.00	2.18	10.1
		9.17	54.33	2.23	10.5
		7.70	40.00	2.16	10.0
		6.02	28.18	2.16	9.9
		4.37	17.23	2.16	10.1
		3.21	10.55	(2.33)	10.4
		2.28	6.64		10.5
	Mean			2.18	10.2

THE ATOMIC WEIGHT OF CHLORINE*

The Ratio NOCl:Ag

BY ARTHUR F. SCOTT AND CLYDE R. JOHNSON

We have investigated a method for the preparation of nitrosyl chloride. From an analysis of this material, purified by fractional distillation in vacuum, the ratio NOCl : Ag has been determined nephelometrically and used to calculate the atomic weight of chlorine.

The formula for the atomic weight of chlorine, using this ratio, is:

$$\text{Atomic Weight Chlorine} = \frac{\text{wt. NOCl}}{\text{wt. Ag}} \times 107.880 - 30.008$$

where the ratio term equals approximately 65.46. An error of one part in 65,000 in determining this ratio by the analysis of nitrosyl chloride causes an error of one part in 35,000 in the calculated atomic weight of chlorine, and places the third decimal place in error by one unit. The three terms in the above equation,—the atomic weight of chlorine, the ratio term, and the term to be subtracted,—are of the same order of magnitude. Mathematically, this represents a favorable condition, and an accurate determination of the NOCl : Ag ratio should give considerable information bearing upon the atomic weight of chlorine. It is of further advantage that only two antecedent atomic weights are needed in the calculation, and that these are among the best known of all of the atomic weights.

A distinct disadvantage in the use of nitrosyl chloride in atomic weight work is the fact that it decomposes photochemically. Kiss[1], and Bowen and Sharp[2] report a decomposition of as much as 10% in the gaseous material in a glass bulb at a pressure corresponding to 456 mm. of mercury, after 10 minutes exposure to the light of a 10 ampere carbon arc. Our own results confirm this observation, and lead us to the conclusion that the photochemical decomposition cannot be neglected, in any exact measurements of the properties of nitrosyl chloride.

It may be mentioned that this compound has been used previously for the determination of the atomic weight of chlorine by Guye and Fluss[3], and Wourtzel[4], who employed unique methods of analysis. In their work no precautions were taken against photochemical decomposition. Therefore, their values for the atomic weight of chlorine are placed in some doubt. Nevertheless, these investigations, and that of Briner and Pylkoff[5], indicate, as we also have found, that under certain conditions nitrosyl chloride can be obtained almost analytically pure, in spite of the photochemical decomposition.

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* Contribution from the Chemistry Department of The Rice Institute.

[1] Kiss: Rec. Trav. chim., 42, 665 (1923).

[2] Bowen and Sharp: J. Chem. Soc., 127, 1026 (1925).

[3] Guye and Fluss: J. Chim. phys., 6, 732 (1908).

[4] Wourtzel: J. Chim. phys., 11, 214 (1913).

[5] Briner and Pylkoff: J. Chim. phys., 10, 640 (1912).

Preparation of Nitrosyl Chloride

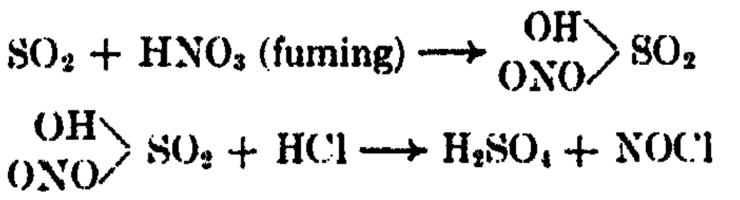
The nitrosyl chloride used in this work was prepared by two methods:

Preparation I. In the first method of preparation, the compound was made by passing pure, dry nitric oxide and chlorine through a 250 ccm. bulb filled with glass baffles, cooled to about −18°C. in an ice-salt mixture. The product was collected in a similar bulb cooled to between −30°C. and −60°C. with a mixture of alcohol and carbon dioxide snow. The chlorine was obtained from a tank of the commercial material. The nitric oxide was prepared by the method due to Winkler[1], and recommended by Moser[2]. Both gases were suitably washed. A current of pure, dry nitrogen was used to sweep the oxygen from the nitric oxide washing train. This gas was obtained by dropping a cold solution of sodium nitrite into a hot solution of ammonium chloride. The preparation was carried out in an apparatus made practically all of glass.

In the final experiment, in which 450 grams of potassium iodide were used in preparing the nitric oxide, 275 ccm. of a mixture of nitrosyl chloride, chlorine, and other undetermined impurities was obtained. This was distilled into fractions in a series of all-glass systems, and analyzed as hereinafter described. The removal of the excess of chlorine in the product by this fractional distillation proceeded so slowly that the above method of preparation was considered unsatisfactory.

Preparation II. The method of preparation finally adopted is a modification of that described by Tilden[3]. Since it has several distinct advantages, and has not previously been described, the method is given in detail below.

Since in any synthesis of nitrosyl chloride the introduction of at least one impurity in the final product is practically unavoidable, we selected the following reactions, in order to get the least objectionable one:



$$SO_2 + HNO_3\ (\text{fuming}) \longrightarrow \begin{matrix} OH \\ ONO \end{matrix}\!\!> SO_2$$

$$\begin{matrix} OH \\ ONO \end{matrix}\!\!> SO_2 + HCl \longrightarrow H_2SO_4 + NOCl$$

The use of hydrogen chloride in place of the usual sodium chloride enables the reactions to be carried out continuously, in a single reaction flask. It also eliminates the possible introduction of certain oxides of nitrogen, which have boiling points undesirably close to that of NOCl. Moreover, the low boiling point of the principal impurity, hydrogen chloride, lends itself to the more ready separation of the two substances by fractional distillation.

The apparatus used in washing the sulfur dioxide and hydrogen chloride, the hydrogen chloride generator, the reaction flask, and the collection apparatus for the NOCl were all of glass, except the connection to the tank of sulfur dioxide. In general, the preparation system consisted of three trains of 12″ × 1″ gas washing towers filled with 1/8″ glass beads moistened with

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[1] Winkler: Ber., 34, 1408 (1901).

[2] Moser: Z. anal. Chem., 50, 401 (1911).

[3] Tilden: J. Chem. Soc., 27, 630 (1874).

the washing solutions, leading into a 3 liter Pyrex reaction flask. Glass stopcocks were placed at convenient points in the gas lines. Air, sulfur dioxide, and hydrogen chloride could be passed through the washing trains and into the reaction flask either above or below the surface of the contained liquid. An outlet tube led from the flask, through a tube of phosphorus pentoxide, a safety bottle, and an aspirator, into a hood. A separatory funnel was connected at the top of the reaction flask.

The sulfur dioxide used in the reaction was passed through six towers of beads containing concentrated sulfuric acid which had been heated to fuming. The hydrogen chloride was generated by dropping concentrated sulfuric acid into concentrated hydrochloric acid, contained in a 3 liter flask. It was passed through four towers of beads containing concentrated sulfuric acid. The air washing train led successively through dilute silver nitrate solution, solid anhydrous calcium chloride, two towers of 1 : 1 sodium hydroxide solution, and three towers of concentrated sulfuric acid. The usual precautions were observed in making up each of the reagents used in washing the gases.

The essential details of the preparation will now be described: Five pounds of c. p. fuming nitric acid were placed in the 3 liter reaction flask. The flask was cooled in a bath of cracked ice, and sulfur dioxide was passed into the liquid below the surface at a moderately rapid rate for about 45 hours, discontinuously. Crystals of nitrosylsulfuric acid gradually separated from the solution, and showed a tendency to clog the outlet and inlet tubes. For this reason the outlet tube was large and contained no stopcocks. Whenever the inlet tube became clogged, it was opened by allowing concentrated sulfuric acid to run into it through the separatory funnel at the top of the reaction flask. None of the nitrosylsulfuric acid crystals entered the apparatus intended for the collection of the nitrosyl chloride, as this system was connected in parallel with the outlet tube by a special glass valve, which was only opened when the collection of the product was about to begin.

Sometime after the crystals began to separate, brown fumes ceased to come from the mixture. The contents of the flask became noticeably lighter, changing rapidly to a white or lemon-yellow color. After this stage had been reached, sulfur dioxide was passed into the reaction flask for another three hours. At the end of this time a small amount of liquid still remained in the flask.

About 200 ccm. of previously boiled concentrated sulfuric acid were added to the mixture in the flask, through the separatory funnel, while air was passing through the flask. At the same time the flask was heated in a water bath to about 100°C. The contents of the flask gradually became liquid. The space above the liquid was filled with brown fumes of nitrogen dioxide, which gradually disappeared. Air was bubbled through the heated mixture for 72 hours more, in order to remove all of the nitric acid and nitrogen dioxide. The liquid in the flask was now a light lemon-yellow color, and the vapor was colorless.

The second step in the preparation was next carried out. The valve leading through the collecting bulbs was opened, and the outlet tube sealed, directing the vapors from the flask through the two bulbs. These had a capacity of about 250 ccm.; they were equipped with special glass valves by which they could subsequently be connected to other all-glass systems.

Dry hydrogen chloride was then passed into the solution of nitrosyl sulfuric acid in sulfuric acid, at a moderately rapid rate. Green-brown fumes of nitrosyl chloride formed in the flask and condensed in the collecting bulbs. The first bulb was cooled with an ice-salt mixture to about −18°C.; the second was cooled to about −25°C. with a mixture of carbon dioxide snow and alcohol.

The bulbs were attached so that they could be removed separately. When the second bulb was about ¾ full, it was sealed off from the inlet tube. Its outlet tube led through drying tubes and safety bottles to an aspirator. Before the outlet tube was sealed, the full suction of the pump was applied, and nitrosyl chloride was allowed to boil away until the bulb was a little over half full, whereupon it was sealed off completely from the air. This bulb was estimated to contain about 150 ccm. of nitrosyl chloride. The second bulb was sealed off similarly with 35 ccm. of the material. The contents of the first bulb were purified by fractional distillation and analyzed as described below.

Distillation of Nitrosyl Chloride

All of the distillations were carried out in evacuated all-glass apparatus, and samples for analysis were collected in small glass bulbs. This apparatus differed in no respect from that used by Baxter and Scott in their work on the boron halides. For the sake of brevity no further description[1] is given, but all essential details of the distillation procedure may be inferred from Table I.

To avoid photochemical decomposition of the NOCl, it was kept in a dark cabinet, except during the actual fractionation process. The last five distillations of Preparation II, however, were carried out in the diffuse red light of a 40 W Mazda lamp reflected through a Wratten Safelight #1, Series 0. The transmitted light covered approximately the range from 5700 to 6400 A. U. According to Magnanini[2], nitrosyl chloride absorbs light in this range, but strong absorption does not occur above 5250 A. U., and there is no absorption between 5650 and 5800 A. U. Furthermore, Bowen and Sharp[3] state that "attempts to show that absorption by the red bands of NOCl lead to dissociation were unsuccessful because of the small amount of light absorbed."

Purification of Reagents

Extreme care was used in purifying the reagents used in this research and suitable tests were made to insure their purity.,

Water, *nitric acid*, and *ammonia* were purified according to the methods given by Baxter and Grover[4]. *Sodium chloride*[5] was twice precipitated from a

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[1] Baxter and Scott: Proc. Am. Acad., **59**, 21 (1923).

[2] Magnanini: Z. physik. Chem., **4**, 427 (1889).

[3] Bowen and Sharp: J. Chem. Soc., **127**, 1026 (1925).

[4] Baxter and Grover: J. Am. Chem. Soc., **37**, 1028 (1915).

[5] Richards and Wells: J. Am. Chem. Soc., **27**, 469 (1905).

saturated solution with hydrogen chloride gas. It was then centrifuged, dried, and finally fused in platinum. *Phosphorus pentoxide* for use in drying the gases used in this work was sublimed in a current of oxygen, according to the directions given by Finch and Peto[1] and Whitaker[2]. *Silver* was prepared by the processes outlined by Baxter and Scott[3], with two deviations from the generally adopted procedure. The use of charcoal was avoided in the first two fusions of the silver, because iron was found present in all of the available samples of this material. The fusions were carried out on a bed of pure lime in an electric furnace constructed as follows: 24 ft. of #18 Chromel "A" wire was wound into a spring on a 3/16 in. iron rod. The coils were sprung apart, wrapped around a 150 ccm. silica beaker, and tied in position with asbestos wicking. The turns were insulated with 1/4 in. blocks of pressed asbestos. The beaker was packed in an earthenware crock with magnesia and sheet asbestos.

The silver was fused in an atmosphere of practically pure methane, which was passed through wash bottles containing alkaline potassium permanganate solution, concentrated sulfuric acid, and cotton. The above described process is considered an improvement over the fusion on charcoal.

The other deviation, which was not regarded as an improvement, was the use of a 16 in. × 1-1/8 in. silica tube in the electric furnace for the final fusion of the silver, rather than the usual length of porcelain tubing.

Four reagents were purified especially for the silver preparation. Ordinary c. p. concentrated *hydrochloric acid*, mixed with an equal volume of water, was distilled through a quartz condenser and the last three-quarters were collected in a quartz flask. C. p. calcium nitrate was carried through the process of purification described by Richards and Wells[4], to pure *calcium oxide*. *Sodium hydroxide* in solution was electrolyzed in a 500 ccm. platinum dish until the passage of a 5-10 ampere current for three hours gave no deposit of iron. Electrolytic *hydrogen* used in the final fusion of silver was passed through towers containing concentrated sulfuric acid, over a red hot tungsten filament, through a 3 ft. tube containing fused sodium hydroxide, and finally over P_2O_5.

The Analyses

The NOCl samples for analysis were in every case contained in sealed glass bulbs of about 5 ccm. capacity. Some were analyzed gravimetrically and others nephelometrically. The gravimetric analyses were used to follow the removal of the excess chlorine from the preparations of nitrosyl chloride, and were carried out in the customary manner[5]. With the exception of the analysis of Bulb #39, the correction for the solubility of the silver chloride in the final washings was omitted (all other corrections were applied), and there-

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[1] Finch and Peto: J. Chem. Soc., 121, 692 (1922).

[2] Whitaker: J. Chem. Soc., 127, 2219 (1925).

[3] Baxter and Scott: Proc. Am. Acad., 59, 23 (1923).

[4] Richards and Wells: J. Am. Chem. Soc., 27, 481 (1905).

[5] See, for example, Harkins and Liggett: J. Phys. Chem., 28, 76 (1924); Baxter and Cooper: Proc. Am. Acad., 59, 248 (1924).

fore the results of these analyses are not fully comparable to those of the nephelometric analyses. The latter analyses were carried out with rigorous adherence to the usual technique, as described in many of the representative atomic weight determinations based on the nephelometric procedure described by Richards and Wells[1].

Since the procedures referred to above are standard, they are not described in detail. We shall note below only important deviations from these procedures and also certain innovations which were found to be advantageous.

Weighings: A #10 Troemner balance and the best grade of lacquered brass weights were used for the weighings. The weights were calibrated just before and after use in this work. Although none employed in the analyses showed a greater change than 0.01 mg., it is interesting to note that the 2.0″ gram and 10.0″ gram weights increased by 0.04 mg. and 0.20 mg., respectively. Weighings were made with precautions to avoid errors greater than 0.02 mg., and for the nephelometric analyses were made in duplicate.

Vacuum corrections were calculated from the usual formula[2], the air density being determined for each case by measurement of the temperature, pressure, and relative humidity. Calibrated instruments were used. This policy was considered advisable in view of fluctuating atmospheric conditions, and was made easier by an ingenious graphical method of calculation, for which we are indebted to Dr. P. F. Weatherill[3].

The densities employed in calculating the vacuum corrections were: Silver, 10.5; Silver chloride, 5.56; Glass, 2.48; Sodium chloride, 2.16; Brass, 8.4. The density of glass was determined in this laboratory from typical samples.

Collection of the Glass Fragments: The transfer of the glass fragments of the sample bulb to the filter, probably the weakest link in the analytical operations, was effected with extreme care. After thorough washing by decantation, the main portion of the fragments was removed to a 400 cc. beaker in the usual manner. The flask was then suspended in a ring with its neck extending downward into the beaker. A jet of water from a wash bottle with an S-shaped nozzle, which reached up into the flask, expedited the washing of the remaining glass fragments into the beaker. By this device the splashing incident upon the use of an ordinary wash bottle was also avoided. The transfer of the glass fragments to the filter paper from the beaker was comparatively easy, because a rubber "policeman" could be used to remove the finer particles.

Finally, in burning away the filter paper care was taken never to fuse the glass, even for check weighings, because it was found that the bubbles which sometimes appear on fusion may expand to an extent sufficient to render the vacuum correction for the glass inaccurate.

Precipitation of Silver Chloride: The filtered chloride solution from the hydrolysis of the NOCl, preparatory to precipitation, contained 50 cc. of

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[1] Richards and Wells: J. Am. Chem. Soc., **27**, 507 (1905).

[2] Landolt-Börnstein's Tabellen, 2nd. ed., p. 15.

[3] Private communication.

concentrated nitric acid. It was precipitated with almost the theoretical amount of silver, which was weighed, dissolved in 40 cc. of 1 : 1 nitric acid in a flask with a Richards' tower, and made up to 600 cc. Contrary to the usual custom, the silver solution was added to the chloride solution through a funnel with a capillary tube, from which it flowed down the side of the 4 liter Pyrex analysis bottle at the rate of about 4 cc. a minute. The final volume after precipitation was approximately two liters.

After precipitation the bottles were first cautiously shaken by rotation, then violently shaken 50 times each day for two weeks before testing with the nephelometer. From this time on they were frequently shaken and tested until the final end-point was reached and checked. The adjustment to the end-point was made with standard solutions containing one milligram of silver or its equivalent of chlorine per milliliter.

Determination of the End-Point: In the course of the present research a study was made of the influence of various factors on the nephelometric end-point. The optimum light intensity, the change in the nephelometer readings per unit addition of chloride and silver ions, the effect of the acid concentration, the degree of precision obtainable, the effect of time following precipitation on the nephelometer readings, and the effect of certain changes in the general procedure, were considered. An outgrowth of this study was the following method of procedure, which apparently gives reproducible results and which was adopted in determining the end-point in the final analyses:

In a room illuminated by red light, 1 ml. each of $AgNO_3$ and NaCl solutions were introduced into test tubes from calibrated 5 ml. burettes. These solutions contained the equivalent of 0.001 gm. of silver per milliliter, and 5 cc. of concentrated HNO_3 per liter. To each of these test tubes there was then added 20 cc. of the saturated supernatant liquid from the analytical solution which was to be tested. After identical stirring, the tubes were placed aside, and examined in the nephelometer two hours after precipitation.

The examination consisted in exposing 65 mm. of the cup containing excess of silver ion, and adjusting the jacket of the other cup until the fields seen in the eyepiece matched. Five readings were taken in which one field was initially brighter, and five in which it was initially darker. The tubes were then reversed and two more sets of five readings each were taken.

Actual adjustment to the final end-point was continued until the average of at least three such readings of the ratio of the exposed heights of the tubes was within 0.03 units of 1.00. The average deviation of such a series was never more than 0.02 units, although individual readings were scattered over a wider range. While the correction to make the ratio 1.00 exactly never amounted to more than 0.03 mg. of silver or its equivalent in chlorine, it was nevertheless calculated for the sake of uniformity. The correction was based on our data which shows that a change of 0.01 unit in the ratio corresponds to the addition of 0.006 mg. of silver per liter of solution. The solutions were kept under observation for at least a month.

In order to check the standard solutions employed, as well as the foregoing nephelometric procedure, five saturated solutions of pure silver chloride containing varying amounts of nitric acid were tested at various times during the nephelometric observations. The average value found for the ratio of the exposed lengths of the tubes was 1.00, with an average deviation of 0.02 units, the individual values varying from 0.94 to 1.05.

The Results

Preparation I of NOCl was never guarded against exposure to light. It was fractionally distilled under varying conditions in five different systems, several more and less volatile fractions being rejected each time. Although no refluxing column was employed during these distillations, an attempt was made to hasten the removal of excess chlorine by taking off low boiling fractions from the material while it was almost completely frozen. In the fifth distillation the main portion was chilled in an ice bath and the samples condensed by means of liquid air. Four of the more volatile samples so collected were carefully analyzed and the percents of chlorine found are given below. The sample numbers give the sequence in which the samples were collected.

Sample No.	14	16	17	18
Percent chlorine	57.20	56.46	56.12	55.68

Preparation II was likewise purified by repeated fractional distillation the essential details of which are summarized in Table I. In this table the term light or dark signifies that the distillation was carried out in white or red light, respectively. At other times the material was always kept in a dark cupboard. The expression refluxing indicates that during the distillation conditions were maintained whereby the nitrosyl chloride was constantly refluxing in a Hempel tower. Column I gives the number of the samples in the order in which they were removed. The designations "head" and "tail" are used in Column II to show whether these samples were more or less volatile fractions; "main" indicates the middle portion which was the initial material of the succeeding distillation. The estimated volume of each sample is given in Column III. The nature of the refrigerant used to condense a sample is stated in Column IV. The figures contained in Column V are the percentages of chlorine found for every sample which was analyzed. The method of analysis, gravimetric or nephelometric, is given in Column VI.

TABLE I

Data bearing on the Purification of Preparation II

First Distillation
(Light)

I	II	III	IV	V	VI
1, 2	head	9.0 cc.	CO_2-alc.		
3	"	5.0 cc.	"	60.05	gravimetric
4	"	4.0 cc.	"		
	main	124.0 cc.	ice-salt		
5	tail	6.0 cc.	CO_2-alc.	54.42	gravimetric
6	"	2.0 cc.	ice-salt		

Table I (Continued)
Data bearing on the Purification of Preparation II

Second Distillation
(Light)

I	II	III	IV	V	VI
7, 8	head	4.5 cc.	liq. air		
9	"	3.5 cc.	"	57.19	gravimetric
10	"	2.5 cc.	"	57.19	gravimetric
11-23	"	39.5 cc.	"		
24	"	3.5 cc.	"	54.59	gravimetric
25	"	3.5 cc.	"		
26	"	4.0 cc.	"	54.35	gravimetric
	main	60.0 cc.	ice-salt		
27	tail	3.0 cc.	"		

Third Distillation
(Light-Refluxing)

28	head	1.0 cc.	liq. air	54.68	gravimetric
29	"	2.0 cc.	"	54.42	gravimetric
30-33	"	3.0 cc.	"		
34	"	2.5 cc.	"	54.238	nephelometric
35	"	2.5 cc.	"	54.217	nephelometric
	main	45.0 cc.	ice-salt		
36	tail	3.5 cc.	liq. air	54.130	nephelometric
37	"	0.5 cc.	ice-salt		

Fourth Distillation
(Dark-Refluxing)

38	head	3.5 cc.	CO_2-alc.	54.22	gravimetric
39	"	3.5 cc.	"	54.166	gravimetric*
	main	35.0 cc.	"		
40	tail	1.0 cc.	"	54.09	gravimetric
41	"	2.0 cc.	ice-salt		

* All solubility corrections were applied in this case.

Fifth Distillation
(Dark-Refluxing)

Unfortunately, at the outset, a capillary in the distillation system was broken, allowing air to enter. Measurements gave as the maximum amounts admitted: 110 cc. of air and 2 cc. of water vapor. About 3 cc. of material were lost in expelling some of the air.

Sixth Distillation
(Dark)

To eliminate some of the air admitted in the above accident a special apparatus was constructed with a total volume of 30 cc. It was so devised that the bulb containing the NOCl, when finally sealed off from the system, had only 0.8 cc. of vapor. A partial fractionation was effected during the transfer.

TABLE I (Continued)

Data bearing on the Purification of Preparation II

I	II	III	IV	V	VI
	main	29.0 cc.	CO_2-alc.		
42	tail	2.0 cc.	ice-salt		
		Seventh Distillation (Dark-Refluxing)			
43	head	1.5 cc.	CO_2-ether	53.97	gravimetric
44	"	1.0 cc.	"	53.92	gravimetric
45	"	4.0 cc.	"	54.19	gravimetric
	main	19.0 cc.	"		
46-47	tail	3.5 cc.	"		
		Eighth Distillation (Dark-Refluxing)			
48	head	3.5 cc.	CO_2-alc.	54.235	nephelometric
49	│	3.0 cc.	"	54.218	nephelometric
50	│	3.0 cc.	"	54.162	nephelometric
51	│	3.0 cc.	"	54.162	nephelometric
52	│	3.0 cc.	"	54.162	nephelometric
53	↓	3.0 cc.	"	54.118	nephelometric
54	tail	0.5 cc.	"	54.079	nephelometric

Our analytical data show that the final 19 cc. portion contained 54.174 percent of chlorine.

Finally, the complete analytical data for the three samples, which presumably contained pure nitrosyl chloride, are given in Table II.

TABLE II

Sample Number	Weight of NOCl in vacuum gm.	Weight of Ag in vacuum gm.	Weight of Ag added or subtracted in solution gm.	Weight of Ag added or subtracted: nephelometer correction gm.
50	3.92308	6.46519	−0.00036	+0.00003
51	4.16219	6.85433	+0.00462	+0.00001
52	4.17839	6.88652	−0.00085	±0.00000

N = 14.008 Ag = 107.880

Sample Number	Corrected weight of Ag in vacuum gm.	Ratio NOCl:Ag	Atomic Weight of chlorine
50	6.46486	0.606832	35.457_0
51	6.85896	0.606825	35.456_3
52	6.88567	0.606824	35.456_2
	Average	0.606827	35.456_5

Discussion of Results

The purity of the nitrosyl chloride in the three samples (#50-#51-#52) is evidenced by the following facts. In the first place these three middle fractions contain sensibly the same percent of chlorine, a condition which can result only when the distilled material is pure or when a constant-boiling mixture is present. The improbability of having a constant boiling mixture which would yield the same value for the atomic weight of chlorine as that obtained by many other methods, is sufficient ground for rejecting the second possibility.

Further evidence for the purity of these samples can be adduced from the manner in which the impurities are removed by fractional distillation. For instance, the data in Table I show that excess hydrogen chloride is reduced with considerable rapidity. The few cases which are exceptions to this statement can doubtless be attributed to photochemical decomposition. Both decomposition products are more volatile than NOCl and are ultimately removed by fractional distillation. The nitric oxide, however, appears to distill off almost as fast as it is formed whereas the more soluble chlorine is not so volatile. That chlorine impurity in NOCl can be removed by fractionation is clearly shown by the data given for the purification of Preparation I.

Additional light is thrown on the question of the elimination of low-boiling impurities by an examination of the data for the last two distillations described in Table I. For these two distillations followed after the unfortunate accident which admitted air into almost pure nitrosyl chloride. The chief impurities introduced as a result of the rupture are: N_2—O_2—HCl—HNO_2. Since the composition of the high boiling fraction before and after the rupture is about the same, we can reasonably assume that only small quantities of HCl and HNO_2 were formed by the hydrolytic reaction. Hence the sequence of the impurities in the above list gives the order not only of decreasing volatility but also of decreasing amounts. If the impurity distills off in the given sequence, we should expect the first portion to be low in chlorine (presence of N_2 and O_2), the second to be high in chlorine (presence of HCl), the third to be pure NOCl, and finally the tail fraction to be low in chlorine again (presence HNO_2). As a matter of fact this is essentially what took place on distillation.

To support the conclusion that low-boiling impurities can be quantitatively removed by fractional distillation we may mention one more fact, the apparent abrupt exhaustion of impurity. This phenomenon is exhibited in two cases: in one case the percent of chlorine in consecutive fractions drops from 54.22 to 54.166: in the other, from 54.218 to 54.162. The theoretical percentage of chlorine in NOCl, is 54.162.

The following conclusions can be drawn regarding the high-boiling impurities. Since the percent of chlorine in the tail fraction of the first distillation is 54.42 and that of the fourth distillation is 54.09, the nitrosyl chloride may have contained at least two impurities with boiling points higher than −6°C. The more volatile of these would have a greater chlorine content than NOCl; the other would contain less chlorine and is probably nitrogen dioxide (bpt. 21°C.). The data in Table I indicate that there is a rather sharp separation of nitrosyl chloride from these impurities on fractional distillation.

Summary

The possibility of determining the atomic weight of chlorine from a measurement of the favorable ratio NOCl : Ag has been investigated.

The analysis of three samples of presumably pure NOCl has yielded for this ratio the value 0.606827 ± 0.0000017, from which the atomic weight of chlorine is calculated to be 35.4565 (N = 14.008 and Ag = 107.880).

An improved method for the preparation and purification of nitrosyl chloride is described. Evidence is offered which indicates that HCl, Cl_2, NO, N_2, O_2, and nitrogen oxides are completely removed from the compound by fractional distillation.

We take great pleasure in acknowledging our indebtedness to the Elizabeth Thompson Science Fund and the Warren Fund of the American Academy of Arts and Sciences, for financial support in this investigation.

Houston, Texas.

1947

THE FORMATION OF PECTIN JELLIES BY SUGAR

BY GENE SPENCER

It has been 150 years since the publishing of the first record found on the jelly-forming constituent of plants. At the end of this time, no theory existed which satisfactorily explained the formation of pectin jelly. The purpose of this investigation has been to study this pectin jelly-formation with a view to deriving a working hypothesis which will explain the facts as we see them and which may serve as a tool in further research on this subject.

Vauquelin[1] started about 1780 to study the substance which he derived from plants and called "gelatin," because it formed a jelly under certain conditions. Thirty-five years later Payne,[2] Guibourt,[3] and Braconnot[4] published papers giving their observations regarding the jelly-forming substances obtained from plants.

Just what substances the men before Braconnot studied is not certain; but it is doubtful if any of them had the pectin which we connect with fruit jellies. Vauquelin's "gelatin" formed a reversible jelly with water; Payne's jelly was insoluble in water; Guibourt's jelly formed spontaneously when certain fruit juices aged.

Braconnot undoubtedly isolated the pectin which we now associate with fruit jellies; but the jellies which he made were in all probability pectic acid jellies and not pectin since his manipulation involved hot treatment with alkalis. Braconnot realized this difference, because in his 1831 paper he said that he had originally thought his jelly was a pectin jelly; but later work showed that this could not be true since "pectic acid is practically insoluble in water, whereas the mucous jelly of fruits which is not acid at all is easily soluble in their juices. These two bodies therefore are by no means identical."

Fifteen years after Braconnot's first paper, Fremy[5] began his investigations starting with the knowledge of how to obtain pectin from fruit juice by alcoholic precipitation, and how to make pectic acid by alkali treatment of pectin. As a result of his work he advanced the first theory for jelly formation. He attributed this formation to the action of "vegetable albumin," (later called pectase), on pectin.

The formation of fruit juice jellies by enzyme action is not uncommon. It probably explains the jellies of some of the earlier workers. But Fremy made the mistake of accounting for sugar jellies in the same way.

Since Fremy, the formation of jellies from fruit juices has been treated in the literature both as a chemical and as a physical phenomenon.

The chemical theories have assumed that pectin jelly-formation involves hydrolysis and, in some cases, the subsequent formation of metallic salts. So far as we have found, the function of sugar, when recognized at all in these theories, has been to give a medium in which the hydrolytic products were insoluble.

Following Fremy, Carles[6] postulated that when a pectin sol was heated a conversion either to insoluble pectic acid or calcium pectate took place. Norris[7] has incorporated this same idea in his textbook. Wendelmuth[8] proposed hydrolysis of methyl pectate as one step in pectin jelly-formation. Halliday and Bailey[9] were somewhat inclined toward the chemical concept of jelly-formation in suggesting that the reason calcium chloride aids in jelly-formation by sugar, is perhaps due to a calcium pectate formation which has a higher jelly forming power than pectin. Tarr,[10] following Loeb and his protein-acid compound hypothesis, suggested a pectin-acid compound forming at a definite pH. Tschirsch[11] is sometimes credited with suggesting a pectin-sugar combination; but actually he was concerned with the peptization of pectin from fruit tissues by means of sugar solution and he did not associate sugar with the mechanism of jelly-formation.

The first attempt to establish pectin jelly-formation as a physical phenomenon was made by Baudrimont in 1844.[12] His work seems to have been totally ignored in subsequent studies of pectin, since no published recognition of Baudrimont's work was found in the pectin literature. Baudrimont's work was discovered by W. A. Bender in his examination of the literature, and Bancroft[13] has given us a paper on "Baudrimont as a Colloid Chemist."

Before discussing further the theories advanced for pectin jelly-formation, we shall consider the constituents which have gradually become recognized as of equal importance with pectin.

More than 100 years after Braconnot announced pectin as the jelly-forming constituent of juices, scientific articles as a whole began to assume the importance of sugar in fruit jelly formation and to assign quantitative limiting values to this constituent.

So little was the importance of sugar in this jelly-making realized that as late as 1911 we find such published statements[14] as . . . "sugar . . . must have little to do with the coagulation property;" and in a text-book[15] as late as 1921 . . . . "many fruits . . . . . contain pectin. These are readily soluble in water, and when dissolved in concentrated solutions in hot water, they set into jellies when the solution is cooled. These jellies carry with them the soluble sugars and flavors which are present in the fruits." Norris[7] also ignores sugar in pectin jelly-making in his text-book.

Beginning with about 1922 several papers were contributed which reported the limiting sugar concentrations for jelly making. Mehlite[16] stated that in his work jellies formed only when the total solids were between 50% and 70%. The minimum sugar requirement reported by Poore[17] was 37%, and by Noyes,[18] was 38%.

Tarr and Baker[19] have compared the strength of jelly with its sugar content and from such data they have plotted a curve which shows a maximum jelly strength at a definite sugar concentration.

It would seem from these observations that the ability of sugar to cause jelly formation diminishes at both high and low concentrations. This impression is confirmed by talking to people who make jelly. The data from Tarr and Baker which corroborate this are shown in Table I.

The third constituent, acid, which has gradually been recognized as an essential of fruit jellies, was first emphasized by the work of Goldthwaite.[10] Various workers have attempted to fix the limiting values for acid in fruit jellies but there is even less agreement in the quantitative figures than in the case of sugar because, as Goldthwaite showed, all acids do not behave identically. This was later confirmed by Tarr.[10]

TABLE I

The relation of % sugar to jelly strength for pectin jellies made by a hot evaporation method, as given by Tarr and Baker.

% Sugar in Jelly	Jelly Strength at top of Jelly (Pressure cm. water)	% Sugar in Jelly	Jelly Strength at top of Jelly (Pressure cm. water)
74.1	63.5	68.5	58.5
72.5	65.5	67.6	55.5
71.4	62.5	66.7	44.5
71.0	67.5	64.5	34.0
69.4	63.5	62.5	28.5
69.0	63.5	60.6	17.5

Tarr and Baker[19] have studied the effect on jelly strength of changing acid concentration. From their data it appears that there is a definite acidity at which jelly forms most strongly. They state: "Increasing the quantity of acid increased the strength of jelly until the optimum jelly was obtained, after which further additions of acid were accompanied by decreasing strength in jellies." Data from Tarr and Baker illustrating this are given in Table II.

TABLE II

The relation of acidity to jelly strength for pectin jellies made by a hot evaporation method, as given by Tarr and Baker.

cc 0.1 N Acid	pH	Jelly Strength Pressure cm. water at top of Jelly	cc 0.1 N Acid	pH	Jelly Strength Pressure cm. water at top of Jelly
3.0	3.65	23.0	9.0	3.24	60.0
3.5	3.60	25.5	10.0	3.19	60.5
4.0	3.53	28.0	11.0	3.16	58.5
5.0	3.46	42.0	12.0	3.13	55.5
6.0	3.38	48.5	13.0	3.11	48.5
7.0	3.33	52.0	14.0	3.08	43.5
8.0	3.28	55.5	20.0	2.94	27.0

The general impression obtained from all people who have studied fruit jelly making is that jelly failure results from either too high or too low acid, and also from too high or too low sugar. In other words the jelly field, between the co-ordinates sugar concentration and acidity, would seem to be a closed field bounded on all sides by a syrup region. The strongest jelly-forming tendency in the field is indicated to be somewhere toward the center of this field.

It is not apparent why sugar should function differently at saturation than it does at concentrations above and below; nor is it clear why both high and low acid concentrations should be less effective in jelly formation than an intermediate concentration. Yet these are the facts as borne out in fruit jelly making, and in the laboratory.

The closed jelly field represents the results obtained from the hot evaporation method. The general technique of this method is given in one of Tarr and Baker's[19] papers: "In making up the jellies, the required amounts of pectin and acid were measured into an agate pan and brought to a boil on an electric plate. Sugar was next added and the boiling continued until that point was reached in the process where the solution showed a tendency to break from a silver spoon in a sheet form. When this "jell point" was observed, the jelly was considered finished and its weight recorded. The finished jelly was then transferred to a jelly glass, covered to prevent evaporation, and allowed to stand for twelve hours at room temperature."

Before accepting the closed jelly field which this method gives, as a basis for developing a working hypothesis for pectin jelly-formation, we decided to find out if the jelly field given by a different method of manipulation would be the same.

Experimental Work

Method of combining Jelly-forming Constituents

Douglas[21] was the first to realize that heating was not an essential for jelly formation. We applied his discovery to this work.

The method devised was to combine the constituents at room temperature as follows: Acid (or alkali) of known strength, and water to make up a definite volume were pipetted into beakers containing a weighed amount of pectin sol of known strength. Definite weights of sugar solution of known concentration were then rapidly mixed with the acidified pectin sol by pouring back and forth between beakers. With very concentrated mixtures, it was necessary to stir the constituents rapidly together with a porcelain spatula, since these jelly mixtures tend to set very quickly.

Very concentrated sugar solutions were required in some of the combinations. Crystallization was prevented in these concentrated solutions as follows: The solutions were prepared in tared beakers by heating a weighed amount of sugar with 10 cc less water than was necessary to give the calculated concentration required for the experiment. The beakers were covered during heating to prevent the concentration of sugar at the top circumference of the liquor. As soon as solution was complete, the beakers were removed from the hot plate and 10 cc of water poured carefully over the top of the solution and the covered beakers carefully set aside to cool. This thin layer of water on the surface successfully prevented crystal formation during cooling. The cooled beaker containing the sugar solution was then put on the balance pan and water added until its weight was brought up to the amount required to give the calculated sugar concentration. The water on the surface was carefully mixed into the sugar solution before it was used. No crystallization ever took place during this mixing.

The time required for the jellies made in this way to set, varied between the instant of mixing and several hours, depending upon the concentration of the constituents. All observations were made 24 hours after mixing, unless otherwise stated.

Acid and Alkaline Range investigated

In addition to studying the acid range, we extended the investigation into the alkaline region.

Belling[33] reported no jelly formation when he neutralized the acid of his mixture before evaporation, with sodium carbonate. Tarr[10] reduced the acidity in his mixtures by adding buffer mixtures and found that between the pH of 3 and 10 no jelly formed. "At a pH of 10, jelly particles scattered through the liquid but no jelly formed that would stand." His explanation of this was .... "This might be due either to the concentration of hydroxyl ions that exist at this pH value, or to the salt concentration which for this particular solution was quite high." Perhaps if Tarr had extended his investigation into the alkaline region no jellies would have formed but it is not certain.

By the cold method, sugar-pectin jellies formed readily in an alkaline medium. That these alkaline jellies represent the same type of formation as the acid jellies and are not a product of chemical decomposition of pectin is evident from four facts: (1) If the alkaline jelly were a result of a chemical change, boiling the mixture should give a more pronounced jelly formation; but experimentally long boiling destroys the jelly-forming tendency of the pectin-alkali-sugar mixture. (2) Under certain conditions of concentration, jellies form instantaneously as do the jellies on the acid side. Since saponification requires time, this argues against a saponification reaction as a preliminary to this jelly formation. (3) We have succeeded in making an acid jelly from pectin recovered from one of these alkali jellies. The process is complicated by the difficulty involved in washing out the alkali before hydrolysis takes place and by the salts resulting from neutralizing the alkali not completely washed out. Especially is this the case in the high alkali, low sugar mixtures. As a result, the remade jelly is weaker than its check acid jelly which was not first converted to an alkali jelly. This is to be expected since it contains either less pectin or more sodium chloride, or both. (4) Alkali of the concentration used in some cases is unable to give a jelly in the absence of sugar or a sugar substitute.

Jelly Field as outlined by this Experimental Work

When the constituents sugar-acid-(or alkali) pectin-water were combined at room temperature, in a series of experiments covering a wide range of acidity (or alkalinity) and sugar concentration, we found a jelly field not only on the acid side of neutrality but also one of somewhat similar shape in the alkaline region. These results are shown qualitatively in Fig. 1.

The quantitative aspects of such a boundary line are meaningless, since the pectin used contained some ash. Electrolyte impurities certainly affect the quantitative value of any work on pectin, making the data specific for the pectin, acid, and alkali used. The pectin impurities should not materially alter the qualitative values, if they are held constant by holding the pectin concentration constant. The acid or base used to adjust acidity or alkalinity will definitely alter the trend of the curve.

Lal Sing's[22] work on pectin jelly gave results of the same nature in the acid region.

From these experiments it is apparent that instead of there being a single sugar-acid-jelly field for pectin, bounded on all sides by a sol region, as we have been led to believe, there are apparently two jelly fields bounded by a sol region on only one side, that is on the low-acid, low-sugar side.

On the high-sugar side, the jelly fields are terminated, theoretically, by the crystallization of sugar, and on the extreme acid and alkaline sides by the decomposition of pectin. Practically, however, the formation of homogeneous pectin jellies at high sugar and high acid (or alkali) concentrations is limited by the mechanical difficulties of getting the constituents mixed before jelly-formation takes place.

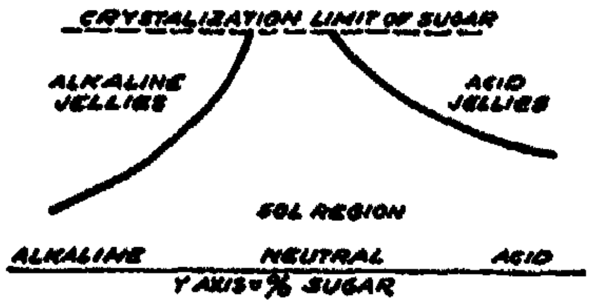

Fig. 1

The relation between the pectin sol and pectin jelly regions in acid, neutral, and alkaline medium resulting from varying amounts of sugar in a given pectin mixture.

The Gel-Sol Boundary Curves with Other Agents than Sugar

The converging tendency of the boundary lines of the acid and alkaline jellies, as shown in Fig. 1, led us to speculate as to the possibility of these two lines meeting, if the barrier of sugar solubility had not interposed; so we tried substituting alcohol for sugar, using the same manipulation as had been used for sugar. The successful making of alcohol jellies, requires rapidity of motion and practice, otherwise one obtains a precipitate and not a homogeneous jelly.

As we anticipated the boundary curve for the alcohol jellies was not frustrated at the high alcohol concentration but was continuous through neutrality.

A few experiments were run using glycerine instead of alcohol and we found that the glycerine boundary curve would lie between the sugar and the alcohol curve. The qualitative relation of the boundary lines of these three precipitating agents is given in Fig. 2.

The effect of pectin concentration on the position of the sugar jelly boundary line on the acid side, was investigated. These experiments showed that as pectin concentration was increased the boundary line fell, that is, the jelly field became increasingly larger with increasing concentration of pectin, Fig. 3.

The continuity of the alcohol jelly boundary curve in Fig. 2 is very important for it must mean that acid is not an essential to pectin jelly-formation, as jelly-making experience has found it to be. The answer to this apparent contradiction is that acid is necessary for pectin jelly only where the jelly forming agent has a low solubility. This point is more readily understood by referring to the boundary curve in Fig. 1. As acidity is increased, a lower sugar concentration is necessary for jelly formation with a given pectin sol.

This lowering of sugar requirement by the presence of acid is fortunate; otherwise it would not be within the solubility limit of sugar, and fruit jellies would not be known.

This does not mean that acid is essential to jelly formation. One could, just as well, have a neutral jelly if the solubility of sugar would permit it, or an alkaline jelly if the epicurean would permit it.

Explanation of Current Opinion on Pectin Jelly-Formation in terms of these Results.

Our ideas on jelly formation are derived from the hot evaporation method. This method has doubtless given valuable information for practical work, but for the study of the theory of gelation it is to be criticized on four points: First, the decomposition of pectin and sugar during cooking. Second, the further loss of quantitative control of the 'constant' constituents because of evaporation. Third, it employs as a jelly-forming agent a substance of limited solubility. Fourth, the possibility of premature precipitation of pectin when the sugar is added to the hot mixture.

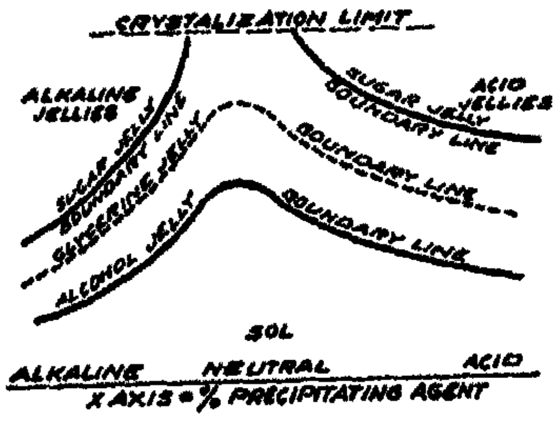

FIG. 2

A qualitative view of the relations of the boundary curves of pectin jelly fields for sugar, glycerine, and alcohol jellies. The alcohol jelly field is the largest, and the sugar jelly field the smallest.

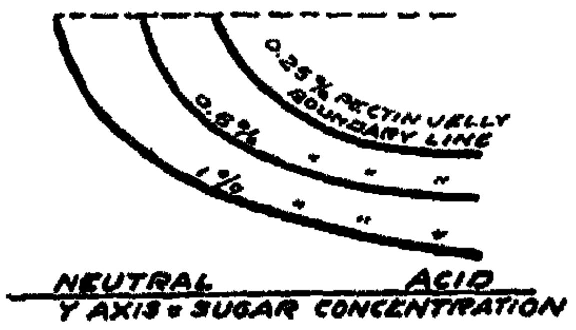

FIG. 3

The relative size of pectin jelly fields for three different pectin concentrations. The 1% pectin jelly field is the largest, and the 0.25% pectin jelly field is the smallest.

When a large amount of cold sugar is added all at once to hot fruit juice which is high in pectin and in acid, the sugar cools the mixture to the point where jelly formation begins before the sugar has had time to dissolve and become distributed through the mixture. As a result of this, particles of pectin in contact with sugar crystals will form small jelly masses. These jelly masses may not be repeptized when the temperature is restored to boiling, so they are no longer available for jelly formation, and this would have the same effect on jelly strength as reducing the pectin in any other way. If this premature precipitation is very pronounced, it gives a mixture which contains thousands of tiny, floating jelly particles rather than a homogeneous liquid which on cooling gives a continuous jelly structure. The jelly-maker describes this failure as "curdling" or "setting in the pan."

That this jelly failure is a purely physical phenomenon may be demonstrated by simply changing the manipulation in mixing the constituents. If the same amount of sugar is added to the same mixture in small increments so as to prevent the cooling of the mixture, the premature jelly formation, as just described, does not take place. The sugar is incorporated and brought into solution without precipitating a part of the pectin and one continuous jelly structure results.

The jelly-strength data showing an "optimum acidity," actually represent a resultant of at least two changes brought about by increasing the hydrogen ion concentration. These two changes affect jelly-formation in opposite directions. It is evident from Fig. 1 that an increase in the acidity of the dispersing medium increases the jelly-forming ability of a given amount of precipitating agent, and so tends to make a firmer jelly; but this same increased acidity also decreases the amount of pectin present by increasing hydrolysis and so tends to make a weaker jelly.

At the "optimum acidity," the weakening effect of acid begins to predominate over the strengthening effect, and with further increase in acid, the jelly strength becomes continuously weaker.

If this hypothesis is correct, a point should eventually be reached in the addition of acid at which the hot method would convert all of the pectin to pectic acid during the cooking process. We would then have an irreversible jelly like Braconnot's original pectic acid jelly and no further addition of acid would greatly alter jelly consistency. We did not work with the hot method so this proof of the hypothesis was not made.

The 3.19 pH turning-point in the jelly-strength curve to which Tarr has given "optimum acidity" significance,—and thence pectin-acid combination significance,—may simply mean that at this hydrogen ion concentration the decomposition of pectin begins to predominate over the increased strength due to increased acidity.

A "minimum hydrogen ion" concentration at which a given pectin-sugar mixture will set to a jelly is in keeping with the gel-sol boundary curve. But it must be recognized that this minimum is specific for each pectin-sugar mixture and does not represent a property of pectin.

Two other expressions which have been used in jelly-making have to do with sugar: one is the "sugar-holding capacity of a pectin sol" or its "sugar worth;" the other is the "optimum sugar concentration."

In regard to the "capacity" or "worth" of pectin Dore[23] states: "At pH 3.37, if the proportion of sugar to pectin is greater than 65:1, the resulting jelly is not firm enough to stand. If the pH be increased to 3.1 it is possible to increase the ratio of sugar to pectin 85 or 90:1."

Tarr and Baker[20] have made a similar statement: "Attention should now be called to the extent to which the capacity of pectin to hold sugar was increased by the hydrogen ion concentration. It will be observed from the data presented in Table I that with a hydrogen ion concentration of pH 3.37, the greatest quantity of sugar that was added to the 2 g. of pectin was 130 g. More sugar than this amount resulted in a jelly that did not have sufficient firmness to stand. However, by inceasing the hydrogen ion concentration to pH 3.23, the sugar holding capacity of the pectin was increased to 145 g. Increasing the hydrogen ion concentration still further to pH 3.10, increased the sugar holding capacity of the pectin to as much as 180 g. The same quantity of pectin (2 g.) has therefore been given more jellying power (30.5 per cent) by increasing the hydrogen ion concentration from pH 3.37 to pH 3.10.

"These relations between pectin and sugar are really measures of jelly strength in which the jellying power of the pectin is shown to be appreciably affected by the hydrogen ion concentration."

The real meaning of this statement is not easy to comprehend so the data given have been transferred from Table I of Tarr and Baker's paper to Table III. The number of grams of tartaric acid required to give the designated pH value to the pectin sol, which they used was obtained from Table III of their paper. The last three columns in this Table were computed by us from the Tarr and Baker data given in the upper half of the table.

TABLE III

		Wt. of Constituents combined			Wt. of finished Jelly
1. Combination Number	2. Wt. of Pectin used (grams)	3. pH	4. Grams Tartaric to give pH designated	5. Wt. of Sugar added (grams)	6.
1	2	3.37	0.1325	130	185.0
2	2	3.23	0.2403	145	202.0
3	2	3.10	0.6230	180	252.0

	Conc. of Constituents in Finished Jelly, calculated from preceding columns		
1. Combination number	7. % Pectin	8. % Tartaric	9. % Sugar
1	1.08	0.07	70.0
2	0.99	0.11	71.3
3	0.79	0.24	71.4

Data basis of the assumption that "the sugar-holding capacity" of pectin is increased by increasing the hydrogen ion concentration.

These data and calculations of Table III show that all of the jellies contain approximately the same amount of sugar, but that the pectin varies by 25% and the acid from 0.07% to 0.24%.

These facts interpreted in terms of the sol and gel fields of Fig. 3 mean that the acid and sugar concentrations (Columns 8 & 9) of Combinations 1, 2, and 3 meet in the gel fields of a 1.08% pectin mixture, a 0.99% pectin mixture, and a 0.79% pectin mixture respectively; but the acid and sugar concentrations of Combination 1 would meet in the sol field of either a 0.99% or a 0.79% pectin mixture. To change the composition of Combination 1 so that it would be in the gel region for either 0.99% or 0.79% pectin, it would be necessary to increase either the acid or the sugar or both. Experimentally, in Tarr's work, this change was made successfully by increasing the acidity from pH 3.37 to 3.23, or to 3.10.

It is thus clear that the phrase "sugar-holding capacity" of pectin is not an expression of some obscure property of pectin, but rather an indication of the relation of acid and sugar concentration to the gel-sol boundary line for that particular pectin mixture. Experimentally it designates how much the acid and pectin of a given sol may be diluted by sugar, and still give a jelly.

In industry, the expression is of practical value in designating the maximum amount of sugar which may be added to a minimum amount of fruit juice (pectin sol) to obtain the maximum yield of jelly of a satisfactory set. Experience has shown that juices differ in their "sugar worth" and thence in their jelly yield. This difference in fruit juices is due chiefly to concentration of pectin, the higher the pectin content the more the juice may be diluted with sugar.

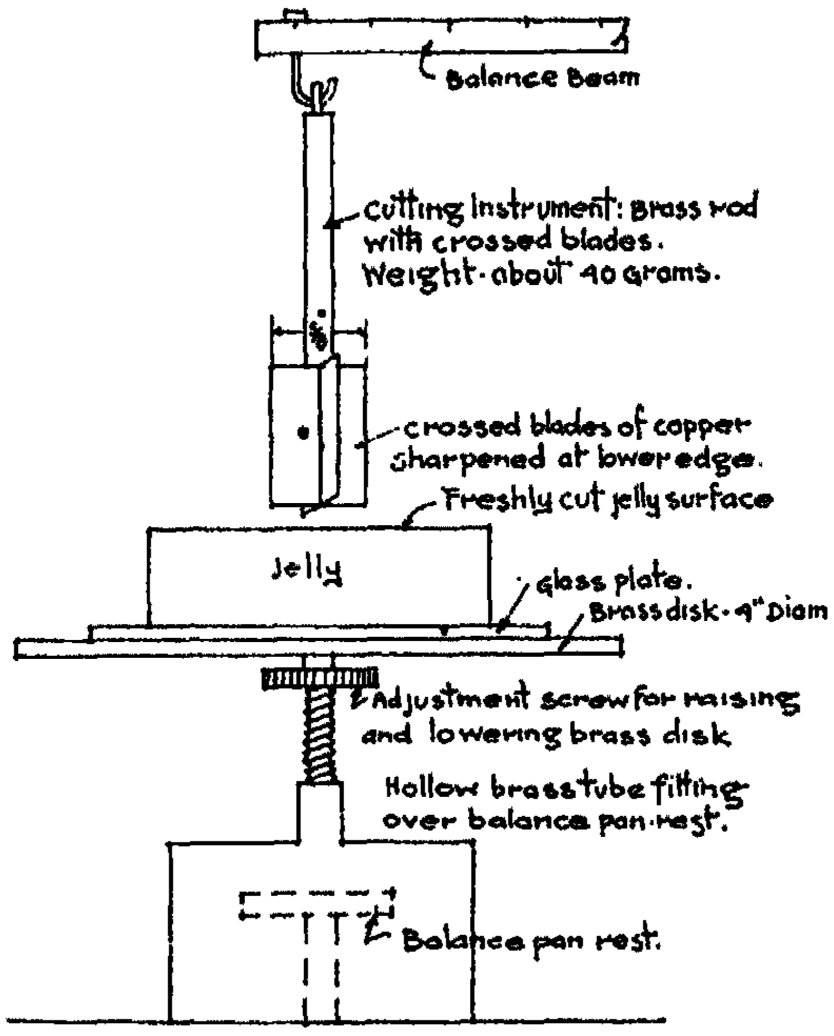

Fig. 4
Jelly-Strength Testing Apparatus

The other factors such as electrolytes, protective colloids, and undoubtedly the nature of the pectin itself which influence the quantitative position of the boundary line, also limit the degree of dilution by sugar permissible for a given pectin sol.

The "optimum sugar" value is, we believe, like the "optimum acidity" a characteristic of the hot evaporation method and not of pectin since by the cold method there is no indication of an optimum sugar concentration independent of other constituents. The error caused by premature precipitation is especially probable in the case of very high sugars.

If this explanation of the optimum acid and sugar values of the hot method is valid, then the cold method which eliminates, almost if not quite entirely, these errors, should be able to demonstrate that jelly strength increases with increasing acidity and with increasing sugar, other constituents remaining constant.

To prove this we made a series of jellies according to the method described above and measured their strength after definite time intervals.

Apparatus: The apparatus, Fig. 4, used for measuring jelly strength was a cutting instrument balanced on the left arm of an analytical balance by means of the ordinary analytical weights. A freshly cut surface of the jelly was brought carefully into contact with the cutting instrument by means of a screw. The minimum weight which, removed from the right balance pan, would cause the cutting instrument to penetrate the jelly, as indicated by the swinging of the needle to the edge of the indicator scale, was taken as criterion of the strength of the jelly. As measured by this apparatus, an ordinary fruit jelly has a strength of from 2 to 4 grams.

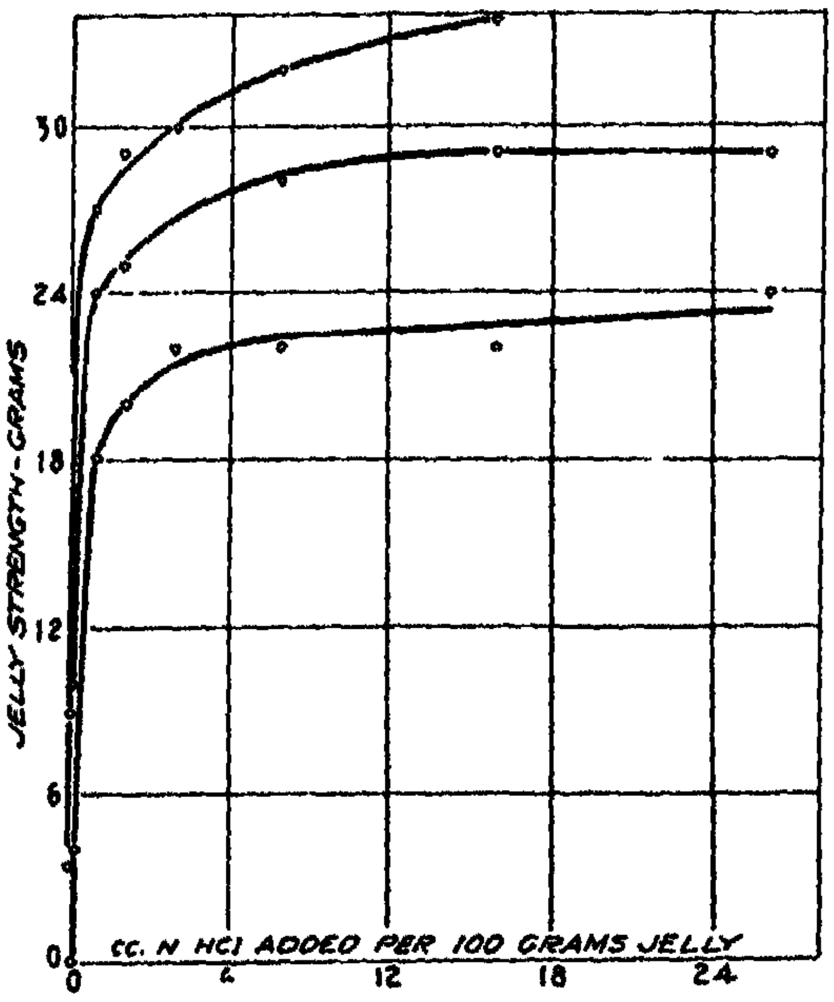

Fig. 5

Acidity against jelly strength for 12 hr., 24 hr., and 48 hr. old pectin jellies containing 1% pectin and 65% sugar.

Results of measurements: Jelly strength measurements were made for a series of jellies in which the changed variable was acidity, the pectin and sugar concentration being held constant. The results are given in Table IV and plotted in Fig. 5.

From the data of Table IV it is seen that there is no tendency for (jelly strength)-(acidity) curves to pass through a maximum when the mixture is made by the cold method.

TABLE IV

Acidity of Jelly expressed as No. cc N HCl per 100 gr. jelly	Weight in grams required to push a sharp blade thru a freshly cut surface of jelly 12 Hrs. old	 24 Hrs. old	 48 Hrs. old
0.0	No jelly	No jelly	3.5
0.2	4.0	10.0	9.0
1.0	18.0	24.0	27.0
2.0	20.0	25.0	29.0
4.0	22.0	—	30.0
8.0	22.0	28.0	32.0
16.0	22.0	29.0	34.0
26.0	24.0	29.0	—

The resistance which jelly offers to cutting increases as the total acidity in the jelly is increased. These jellies contained 1% pectin and 65% sugar.

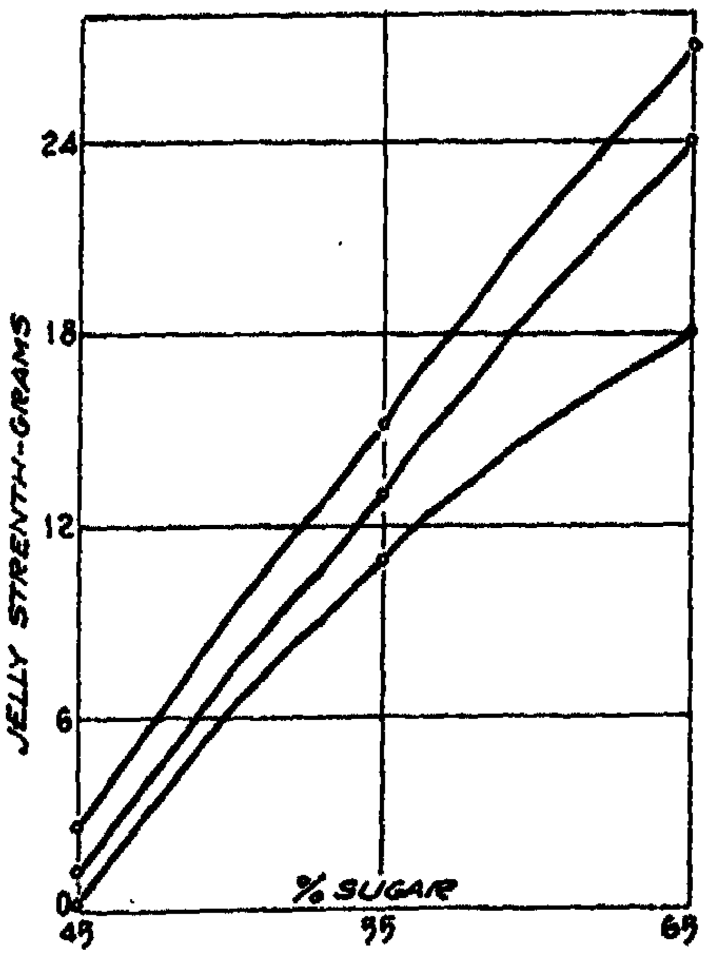

FIG. 6

Percent sugar against jelly strength for 12 Hr., 24 Hr., and 48 Hr. old pectin jelly containing 1% pectin, and 1 cc N HCl per 100 grams.

In the jellies of the second series (Table V, Fig. 6) the pectin and acid were held constant and the sugar concentration changed.

TABLE V

% Sugar in jelly	Wt. in grams necessary to cut thru a freshly exposed surface of jelly 12 Hrs. old	 24 Hrs. old	 48 Hrs. old
45	0.2	1.2	2.6
55	13.0	15.0	17.2
65	18.0	24.0	27.0
(75)	(20.0)	—	(30.0)

The resistance which jelly offers to cutting increases as the sugar concentration is increased. These jellies contained 1 gram of pectin and 1 cc N HCl per 100 grams of jelly.

In the mixtures containing 75% sugar, jelly formation took place before the mixing was completed, yielding a tough, elastic mass full of air bubbles. The last row of data does not, therefore, represent correctly a 75% sugar jelly for the structure is not that of a typical homogeneous jelly.

Crystallization frequently took place soon after mixing was completed for sugar concentrations greater than 70%.

These experiments have shown that the tendency toward a closed acid jelly field with its optimum sugar and acid concentrations in the center, does not represent the colloid behavior of pectin but rather that it is characteristic of the hot evaporation method and need not, therefore, be considered in a jelly-formation hypothesis. In fact, pectin jelly formation by sugar even by the cold method is too specific a case to use by itself as a basis for an hypothesis because of the limit placed by the solubility of sugar.

The colloid behavior of pectin, as regards jelly formation is represented we believe by a continuous jelly field passing through neutrality according to the boundary curves of Fig. 2.

Cataphoresis Experiments and Electrical Charge on Pectin

Before we undertake the formulation of this hypothesis for jelly formation, another set of experiments must be considered which have to do with the electrical charge on pectin.

Since the gel-sol boundary curves (Fig. 2) have a maximum in the region of neutrality, we conducted a series of cataphoresis experiments, using the Mitchell apparatus, to see if this maximum represented an iso-electric point. These experiments showed that pectin is negatively charged in both acid and alkaline media.

Inasmuch as the recognized source of electrical charge in colloid sols is that of the adsorbed ions, it follows that pectin must tend to adsorb anions preferentially to cations, even to hydrogen ions under most conditions. From work which has been done with certain other colloids, a positive charge in acid medium and a negative charge in alkaline medium, might have been expected.

This is not the first case reported of a colloid adsorbing anions preferentially in the presence of excess hydrogen ions. Odén,[24] for instance, has observed it in the case of colloidal sulphur.

Theoretically a reversal of charge should result when anion adsorption is low as compared with cation adsorption.

Experimentally reversal of charge from negative to positive is not easily accomplished because of the very marked anion adsorption preference of pectin. In two instances we were able to bring about this reversal; in one case by treating purified pectin (0.12% ash) with nitric acid, and in the other case by treating with barium chloride.

To make positively charged pectin with barium chloride, a jelly-like precipitate was first formed by neutralizing the stabilizing anion charge with barium ions of barium chloride. The jelly so formed was next macerated in a mortar with crystalline barium chloride. In this way, the barium ion concentration was built up and there resulted a positively-charged viscous sol, which migrated to the cathode in a cataphoresis.

The process of obtaining a positively charged sol with nitric acid did not have this intermediate formation of jelly. In fact, we have never obtained an unquestionable "pectin" jelly by treating a sol with acid. It is true that if the acidity is increased sufficiently, a jelly forms in time; but the jelly is probably a pectic acid jelly since it cannot be brought back into sol form by repeated washing out of the acid with water. In the case of barium chloride jelly a reversal to the sol form is accomplished readily when barium chloride is washed out of jelly.

Professor Bancroft suggested that it might have been possible to obtain a sufficiently high hydrogen ion concentration to destabilize a pectin sol, without the complication of hydrolysis, if one had worked at a very low temperature.

From the fact that we were able to get reversal of charge with nitric acid but not with hydrochloric, we conclude that the nitrate ion is adsorbed less strongly than the chloride ion; consequently the nitrate-stabilized sol is more susceptible to the electrical neutralization and reversal of charge by the action of the cations present, than a sol stabilized by adsorbed chloride ions.

It is interesting to note in connection with the negative charge on pectin that Kopanzenski[25] found pectin to be toxic to living cells. Poisoned cells showed a coagulation of protoplasm when subjected to ultra-microscopic observations. Starch, another negatively charged colloid, is said to produce the same effect.

The soft jelly which Griggs and Johnson[26] report as forming on the cathode immersed in electrolyte-low sols, is presumably due to the excess alkali which had accumulated there and does not indicate a positively charged pectin sol. In our work the jelly which formed at the cathode had the properties of non-peptizability by water characteristic of pectic acid.

The Acidity of a Pectin Sol explained by Anion Adsorption

If no electrolytes are present pectin could still obtain its negative charge from the hydroxyl ions of the water molecule. This would account for the fact that a water sol of pectin normally gives an acid reaction. Bancroft[27] has taken up the effect of adsorption on the acidity of a sol: "If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper or to phenolphthalein, showing that no soluble base or acid is present. If fuller's earth be shaken with a sodium chloride solution and filtered the filtrate is acid to litmus or phenolphthalein. This is because fuller's earth has adsorbed the base. If one presses litmus paper against moistened fuller's earth the litmus paper turns red, and if one adds fuller's earth to a faintly alkaline solution of phenolphthalein, the red color disappears. This is not because the fuller's earth is acid but because it takes the base from the sodium chloride, the litmus or the phenolphthalein.

"I have been told that the adsorbing power of fuller's earth is so great that an acre-foot as soil would adsorb 30,000 pounds of lime and that this would make fuller's earth about equivalent in acidity to a 2% sulphuric acid solution.

"Miss Masters has shown that purified cotton adsorbs some of the base from a sodium chloride solution leaving the solution slightly acid. The alkali can then be washed out of the cotton and the process repeated indefinitely."

This adsorption phenomenon would occur regardless of the chemical nature of the colloid, and might mask or cause an erroneous interpretation of reactions designed to show the chemical nature of the pectin molecule.

For instance the apparent mutual precipitation of the two negative sols, starch and pectin, could be misinterpreted, to signify a chemical union between these two carbohydrates. Gill[28] has reported that starch is precipitated by small amounts of acid; and as stated above, a pectin sol is normally acid. Furthermore, this precipitation of pectin and starch mixtures takes place almost immediately upon mixing the two sols, a behavior not in accord with the formation of organic compounds. That pectin is found qualitatively in the precipitate, together with starch is probably due to the mechanical taking down of pectin by starch, just as coagulating albumin clarifies a turbid medium.

Development of a Working Hypothesis for Pectin Jelly-Formation

Pectin Jelly-Formation a Colloid Precipitation

The first postulate which we make for pectin jelly-formation is that it is a precipitation phenomenon, and not one of those swellings which is said to result in a cellular structure.

The "swelling" hypothesis for fruit jelly-formation is, we believe, very readily disproved by a study of the action of alcohol on pectin.

We are assuming that, since alcohol, glycerine, and sugar all give the same type of jellies, the mechanism by which these agents function is the same. Alcohol is chosen in this discussion in place of sugar or glycerine because the viscosity of the mother liquor is low and so the results are more pronounced and obvious.

When a given pectin sol is treated with a definite amount of alcohol one may obtain by simply varying the manipulation either a firm jelly, capable of being molded from its container, or a precipitate. When the constituents are well mixed before the "set" takes place, a jelly results; when the "set" begins before mixing is complete, a shapeless mass results. This mass is unquestionably a "precipitate" occluding the mother liquor which to a large degree, may be pressed out mechanically. There is no reason to suppose that the mechanism of the alcohol action would differ with the technique of combining the constituents, so alcohol jellies, and hence sugar and glycerine jellies must owe their structure to precipitated pectin.

Another proof that the action of alcohol is one of precipitation is shown even more forcibly when an acidulated pectin sol is allowed to run through a pin hole into absolute alcohol. Under these conditions thread-like streamers of pectin form through the alcohol, very similar in appearance to the formation of artificial silk fibres coagulated from cellulose sol.

Still another indication that the pectin in a fruit jelly is in a precipitated state and not in a "swollen" state is that the mother liquor can be washed out by other non-peptizing liquids without injury to the jelly structure. For instance, a sugar jelly may be converted into an alcohol jelly by simply immersing it in a series of alcohol solutions in which the alcohol concentration is increased with each new immersion. The process can then be reversed by treating this alcohol jelly with sugar solutions of increasing concentration. In the same way the alcohol jelly may be converted into a chloroform jelly, the chloroform into a xylene, and the xylene into a paraffin jelly.

It is difficult to see how xylene which does not in itself precipitate pectin could be incorporated in the jelly structure by simple immersion, if the process were anything more than the washing out of one liquid, from the inter-pectin spaces, by another liquid.

It would be interesting to examine microscopically stained slides made from the "paraffin-pectin" jelly.

The cellular structure of pectin jellies is opposed by Sucharipa[29] who has shown that the solid part of the jelly contains pectin only, and that the liquid contains all the sugar and acid with traces of pectin and methyl alcohol.

Peptization and Stabilization of Pectin Sol

The second postulate has to do with stabilization of pectin in the sol form. We know that pectin adsorbs water and we know that even in very acid medium it migrates to the anode in cataphoresis. Pectin must then be stabilized by adsorbed water and by adsorbed anion.

Precipitation of Pectin

The third postulate is concerned with the mechanism by which the sol is destabilized during precipitation.

When pectin is peptized by water it must be true that an equilibrium is reached between the partial pressure of the adsorbed water and that in the dispersing medium. Precipitation of pectin must disturb this equilibrium in the direction to give pectin in its original unpeptized state. In accord with this, the postulate is made that the precipitating action of organic agents is due to the fact that when they dissolve in the dispersing medium they lower its vapor pressure and, as a result, the adsorbed water which has been stabilizing the pectin, distills, as it were, to the region of lower pressure. This leaves the pectin destabilized and subject to agglomeration. The larger the amount of a given organic agent dissolved in the dispersing medium, the greater will be its precipitating influence, since the greater will be the reduction in the partial pressure of the dispersing medium.

There is nothing new in this idea of sugar affecting the distribution of water between pectin and its dispersing medium. Baudrimont[12] definitely advanced this hypothesis in 1844. "In the preparation of currant jelly, this product shows a consistency varying with the relations existing between the fruit and the sugar which is added to it. With two parts of currants and one part sugar, one obtains a very hard and firm jelly; if the amount of sugar is increased, the pectin is gradually eliminated from the solution, thereby assuming a conspicuous and grainy state so that the firmness of the jelly is considerably decreased.

"In this reaction which is quite specific, it is probable that the particles of pectin swell up, by adsorbing water charged with sugar, thus acquiring a large volume and adhering firmly to one another; but, when the quantity of sugar is increased, a sort of equilibrium tends to be established between the actions which the pectin and the sugar exert on the water present, with the result that the pectin decreases in volume and becomes isolated in particles which float in the sugar syrup. Since the density of these particles is less than that of the liquid, they come to the surface as a sort of scum which may then be easily separated."

Baudrimont assumed that the sugar concentration was highest in those jellies made by adding the largest amount of sugar to the fruit juice before its evaporation, which, of course, is not necessarily true; he also pictured normal jelly formation as a swelling process and jelly failure as a result of a shrinking process. This would give two different behaviors for sugar under the same conditions which does not seem probable.

It is nevertheless probable that if work on pectin jellies had started eighty-six years ago with Baudrimont's suggestion on sugar, our knowledge of pectin jellies would be much advanced.

Bancroft[13] has said of this neglect of Baudrimont's work: "I hope that these quotations will show that Baudrimont was not a man to be forgotten profitably, even though his work along these lines had absolutely no effect so far as we now know. It is a discouraging point of view; but apparently a good idea at the wrong time or by the wrong man, which is perhaps the same thing, is apparently as much wasted as though it had never occurred. One can console oneself, however, by assuming that if it were not for these preliminary and apparently futile efforts, the right time and the right man would never come. Emerson did not love the Irishman but he thought up a use even for him."

That Baudrimont's idea of the transfer of water from pectin to sugar solution actually takes place may be seen experimentally by observing the convection currants resulting from the dilution of a sugar solution in which is immersed a mass of pectin-water paste. The pectin mass becomes transparent but does not swell under these conditions.

In accord with this water-transfer idea we have found that it is impossible to peptize our dry pectin satisfactorily in a dispersing medium containing more than approximately 30% sugar. This is approximately the minimum amount of sugar which we have found capable of bringing about jelly formation with a 1% pectin sol.

The explanation of these experiments, according to our hypothesis of sugar function, is that the dissolved sugar decreases the partial pressure of water. There is then less tendency for water to pass from the dispersing medium to the pectin or, in other words, the pectin would adsorb less water. This decrease in the water adsorption of pectin would become more pronounced as the vapor pressure of the dispersing medium is decreased by the increase in sugar concentration. This would also account in part for the relative positions of the sugar, glycerine, alcohol boundary curves (Fig. 2) since a 40% alcohol solution, for instance, will lower the vapor pressure of water more than a 40% sugar solution. The relative positions of the boundary curves would be reversed if the concentration had been expressed in molar values instead of percentage.

This view of the function of sugar in connection with the water distribution is in harmony with the view held by many workers. Holmes[30] has definitely called sugar a dehydrating agent and classed it with glycerine and calcium chloride in this respect, since all three precipitate pectin. McNair[31] gives a second function to sugar which doubtless has to do with syneresis; that is, its effect on the viscosity of the mother liquor. We know that high-sugar jellies are less subject to syneresis than low-sugar jellies, pectin and acid being constant. Wendelmuth[9] observed that jelly formation increases either as a result of adding sugar or removing water, as by evaporation.

Sucharipa[29] states that pectin is only slightly soluble in the sucrose-acid medium of certain concentrations; but this does not stand as the whole explanation of jelly formation, since a given sucrose-acid medium will give a jelly with one pectin concentration and no jelly with another.

Function of Sugar in neutralizing the Stabilizing Negative Charge

The work which has been done on the precipitation of negatively charged colloids by alcohol has been given by Bancroft[32]: "It seems to be true experimentally that alcohol tends to precipitate negatively charged sols, being more effective if the sol has been made relatively instable by the addition of electrolytes. The negatively charged globules in rubber latex can be precipitated by alcohol in the presence of salts. Thaer states that negatively charged humus is precipitated by alcohol if the concentration of electrolytes is not too low, while van Bemmelen found that alcohol peptizes humus when the latter is charged positively by the addition of acid. Rona and György report that the rate of sedimentation of negatively charged kaolin is increased by the addition of alcohol. Klein has made some rather unsatisfactory experiments to show partial agglomeration by alcohols of negatively charged arsenic sulphide, gold, silica, and ferric oxide, while no agglomeration was obtained with positively charged ferric oxide or alumina. More striking results would have been obtained if Klein had added electrolytes to sensitize the sols.

"Swezey had no difficulty in changing the color of red gold sols to blue and then precipitating them by adding methanol or ethyl alcohol. Methanol is more effective than ethyl alcohol and the effectiveness of both is increased by the addition of sodium chloride. Colloidal silver and an alkaline silica sol were both precipitated by alcohol."

It seems reasonable to suppose that if alcohol is capable of precipitating other negatively charged colloids it would also be capable of neutralizing the negative charge of pectin sols and so tend to precipitate them. For this reason, in addition to its ability to precipitate pectin by its influence on the water distribution, alcohol is probably capable of destabilizing the electrically charged pectin.

No record was found of the precipitation of negatively charged colloid by sugar or glycerine. Whether or not this is such an example cannot be stated. It is experimentally possible to sensitize pectin sols by certain electrolytes so that they require less of each of these precipitating agents.

The Function of Acids and Bases

The fourth postulate has to do with the function of acid and base in pectin jelly formation.

Cataphoresis experiments showing the negative charge of pectin in both acid and alkaline medium have precluded the possibility of explaining the shape of the boundary curve on a basis of isoelectric precipitation or on any other wholly electrical charge basis.

The other stabilizing factor in a pectin sol, aside from its negative charge, is adsorbed water. As has been stated, a vapor pressure equilibrium must exist between the adsorbed water and the water of the dispersing medium. By hypothesis, the underlying principle of jelly-formation by added organic precipitating agents, is the shifting of this equilibrium so that the pectin sol is destabilized, and, under proper conditions, agglomerated to a jelly form.

Since, by experiment, the addition of hydrogen ions on the acid side of the maximum, or hydroxyl ions on the alkaline side, decreases the amount of organic precipitating agent required to cause jelly formation, it follows as a corollary to the sugar-function hypothesis that both acid and base tend to decrease the amount of water adsorbed by the pectin. The maximum water adsorption for pectin is then, by hypothesis, in the vicinity of neutrality and the function of added hydrogen and hydroxyl ions on the acid and alkaline sides of this maximum is to decrease the amount of water adsorbed by the pectin, thus making it possible for a lower concentration of precipitating agents to destabilize the sol and bring about jelly formation.

Conditions under which Pectin Jelly forms

The last postulate considers the factors which determine where the sol region shall end and the jelly field shall begin, and also why there is a distinct jelly field for each concentration of pectin.

It was stated above that the destabilization of a pectin sol would result in a jelly formation "under proper conditions." These conditions are postulated to be those which give an agglomerated net-work capable of supporting the weight of the mother liquor. The supporting strength of any net work structure would seem logically to depend upon two factors,—the continuity of the structure and the rigidity of the structure.

Continuity of structure, by hypothesis, depends upon the number and proximity of pectin particles at the time of precipitation and this in turn is determined by pectin concentration and dispersion.

Rigidity of structure, by hypothesis, depends upon the precipitating tendency of the dispersing medium and this is determined by sugar concentration and hydrogen (or hydroxyl) ion concentration.

If the jelly structure is dependent on the frequency of pectin particles for its continuity, and on acid and sugar concentration for its rigidity, it should be possible to make a jelly of any desired strength by a variety of combinations of the three constituents,—pectin, sugar and acid. A high pectin, low sugar and acid mixture would yield a dense structure, retaining a relatively large amount of absorbed water. A low pectin, high sugar and acid mixture would give a less dense structure but a more rigid one. The hypothesis is borne out experimentally as is shown by the data of Table VI.

TABLE VI

Jelly strength in grams	Composition of mixtures which yield jellies of the strengths indicated		
	Pectin (%)	Sugar (%)	Acid (cc. N HCl/100 grams Jelly)
0.3	0.25	55	0.2
	0.5	45	1.0
1.3	0.25	55	1.0
	0.5	45	16.0
	1.0	45	1.0
4.4	0.5	55	1.0
	1.0	45	8.0

Various combinations of acid, pectin and sugar which will give 24 hour old jellies of the same strength. (In terms of fruit jellies, 0.3 grams of strength is a "very weak jelly" and 4.4 grams strength is a "tough jelly.")

According to these data, a jelly exerting, for instance, a 1.3 gram resistance to being cut may be obtained from a continuity of structure represented by either 0.25% pectin, 0.5% pectin, or 1% pectin. For this to be true, the lower pectin structures would have to be more rigid than the 1% pectin structure. By hypothesis, differences in rigidity are due to the amount of water retained by the pectin at the equilibrium established during precipitation. According to the hypothesis advanced for the function of sugar, this relative rigidity would be determined by the concentration of sugar, the acidity factor remaining constant, or by the concentration of acid, the sugar concentration remaining constant.

The only difference in the composition of the 0.25% and 1.0% jellies of strength 1.3 grams is the concentration of sugar; the lower pectin jelly contains 55% sugar and the higher pectin jelly only 45% sugar. When the sugar concentration was constant at 45%, less acid was required by the 1.0% pectin than by the 15% pectin to give jelly of strength 1.3 grams.

Another example of the influence which acid has on the vapor pressure relations in a mixture is indicated by a comparison of the jelly strength of any two combinations having the same sugar and pectin concentration but different acidities. For instance, the 0.5% pectin jellies containing 45% sugar had a strength of 0.3 grams and of 1.3 grams. This difference in strength is explained by the postulate that excess hydrogen ion decreases the amount of water adsorbed by pectin. The 0.3 grams jellies contained only 1.0 cc acid as against the 16.0 cc. acid of the 1.3 grams jellies. The 45 grams of sugar reduced the vapor pressure of the dispersing medium to the same degree in both mixtures and so was capable of removing the same amount of adsorbed water. The pectin of the high acid mixture, however, held less adsorbed water than the low acid mixtures, so there was less water to remove; the resulting pectin structure for the 16.0 cc acid jelly was more rigid than that of the less acid mixture.

The increase of jelly strength with age, as shown in Table IV is another corroboration of this hypothesis. The adjustment between the vapor pressure of the two phases requires time to reach a full equilibrium. The jellies should accordingly become firmer with time as the system progresses toward its equilibrium. Another factor in this ageing is doubtless the coalescence of overlapping filaments, as has been described for silica jellies by Bancroft.

It is interesting to note that increase in strength becomes less pronounced as time goes on. Jellies of this series kept for six months longer than the others had not increased in strength as much during this time as their duplicates increased during the first forty-eight hours.

Application of this Hypothesis to Fruit Juice Jelly-Making

If fruit jelly is made by evaporating the mixture, it is boiled until some end point is reached, such as the "sheeting-off" (from a spoon) test, boiling-point, or specific gravity. Tarr has shown the spoon or "sheeting-off" test to be unreliable: a series of seven jellies which were evaporated to this point showed consistencies described as "very tough," "tough," "good," a "little tough," "excellent," "good," "soft," "unstable."

Tarr also shows data from a series of fifteen jellies in which mixtures of different composition were heated to the "sheeting-off" point. The weights of the finished jellies were taken and the percentage sugar in each calculated. In the fifteen jellies, the variation in sugar was between 69.4% and 72.7%. From this he concludes that the amount of sugar in jelly made by this method is "a constant within a reasonable limit of error."

From this we learn that the sheeting-off test, like the other tests used as end-points in jelly-making, (the boiling point and the specific gravity), represents chiefly a sugar concentration.

Since the sugar is more or less constant in these hot evaporated mixtures, the question of whether or not a jelly so made will set, depends upon whether or not the acid concentration in the final mixture will meet the sugar concentration, within the jelly field of that particular mixture (Fig. 1). If these two concentrations do intersect in the jelly field the mixture will set; if not, the mixture remains "syrup."

The softest jellies in a given jelly field are those of which the sugar-acid concentrations lie along the boundary line. Tougher jellies result when the concentrations are further from the line in the jelly field. (Mixtures, the composition of which lies within the jelly field, but which, because of premature precipitation do not have an opportunity of forming a jelly normally, and so are very soft, need not confuse this discussion).

Where the gel-sol boundary line for a given cooked jelly mixture will lie, depends first upon the amount and condition of pectin and protective colloids present in the original juice; second whether conditions in the cooking mixture favored decomposition of pectin during evaporation; and third, on the electrolytes characteristic of the juice.

The quantitative values for the gel-sol boundary line are specific for each fruit. The cranberry jelly field was the largest of all fruit studied. The apple jelly field was smaller, and the strawberry and elderberry jelly field are still smaller,—strawberry because of low pectin, elderberry probably because of the presence of salts or protective colloids which tend to stabilize the sol.

Naturally, the larger the jelly field the easier it is to make jelly, since the larger the jelly field the larger the range of sugar and acid concentrations possible. When the jelly field is small, it is much easier to miss it, and end with a mixture the composition of which puts it in the sol region for that particular fruit.

Within the jelly field for every fruit is a sugar-acid concentration which will yield a jelly of whatever characteristics desired. Hitting upon this point by the evaporation method of jelly-making, is a matter of luck; it may be arrived at with some precision by the use of commercial pectin and formulae based on a knowledge of the characteristics of each specific fruit.

In fruit-jelly parlance, failures caused by either "too much" or "too little" sugar, may refer (1) to the failure of the jelly to set, (2) to a premature set, or (3) to a too tough jelly. The matter is further complicated by the fact that the designated amount of sugar sometimes refers to that added to the hot juice and sometimes to the sugar in the finished jelly.

Failure of a jelly to set means that the acid-sugar concentrations are outside the jelly field for that fruit. Before it will set, either these concentrations must be moved into the jelly field or the jelly field must be enlarged until the original acid-sugar concentrations are included within it. This enlargement of the jelly field is most obviously done by adding more pectin. It could undoubtedly be enlarged by adding to the juice certain salts or other substances which tend to destabilize the pectin but no work from a practical standpoint has ever been done so far as we know along this line.

The premature-set failure probably would have been one variety of a "tough jelly" if the setting had been delayed until the hot mixture were in the glasses. These mixtures in which the pectin is precipitated the instant the constituents are mixed are those the composition of which lies well within the jelly field. One of these failures can be remade into a satisfactory jelly by shifting its composition back into the sol field and then bringing the composition back into the gel region.

This shifting from the gel to the sol fields may be accomplished either by reducing the acidity of the jelly by mixing in completely a small amount of alkali, or by adding water, thus reducing the concentration of both acid and sugar. This also dilutes the pectin enlarging the sol field for that particular mixture.

After the addition of the peptizing agent, the mixture must stand with frequent stirring long enough for the pectin to be well peptized. Then if the peptizing agent was an alkali, acid is added to restore the mixture to the jelly field. If water was used instead of alkali to bring the mixture into the sol region, then the repeptized mixture would need to be evaporated until its composition was returned to the jelly field. More pectin, sugar, and acid could be added and evaporation omitted to accomplish this same purpose.

We have accomplished these reversals from gel to sol, and back again with currant jelly, by both of these methods. Each time the process is reversed, the jelly is of course weaker—because of the unavoidable experimental error introduced by heating the pectin sol—in the one case or in the other by the salts formed in the mixture when the acidity is shifted between the gel and sol region.

This weakness may be overcome entirely by increasing the concentration of any one of the constituents; an increase in either the sugar or the acid would move the composition of the mixture further into the jelly field and so make the jelly stronger; or the same thing could be accomplished by enlarging the jelly field by adding pectin.

The successful application of this hypothesis to such a difficult problem as remaking a jelly which has once set, is a very encouraging evidence of its correctness.

It should be possible, according to this hypothesis, to peptize a fruit jelly which has once set, by heating it sufficiently under a very efficient reflux condenser, so that there would be no loss of water. The jelly so peptized should then set again on cooling. The remade jelly would of course be weaker than the original because there would be some pectin loss; but it would seem that enough pectin should be left to show a jelly formation. We have not as yet tried this.

The jelly failure which is called "too tough" results from a mixture which is too far from the gel-sol boundary line. This, according to jelly makers, is usually caused by too little sugar. They do not mean too little sugar in the final jelly, they mean that too little sugar was added to the fruit juice so that by the time the "spoon test" was reached,—according to Tarr, by the time enough water had been evaporated to bring the sugar concentration up to saturation point,—the pectin had also been concentrated and the jelly field unduly enlarged. As a result the acid-sugar composition of the mixture when it finally gave the sheeting-off test, was far from the boundary line instead of rather close to it, as it should be if a tender jelly is to result.

Failures caused by adding "too much" sugar to the original juice are just the reverse. The saturation point of sugar is reached before the pectin is sufficiently concentrated. If evaporation were continued until the pectin is sufficiently concentrated, crystallization would result,—which is still another variety of jelly failure.

Summary

The hot evaporation method of pectin jelly-making is limited by its unavoidable experimental errors and by the low solubility of sugar.

A cold method using several precipitating agents is recommended for theoretical studies of pectin jellies. When this method is used and the so found minimum jelly-forming concentrations of acid (or alkali) and precipitating agent are plotted on co-ordinate paper, a continuous gel-sol boundary line results with its maximum precipitating agent concentration in the vicinity of neutrality. The solubility limit of sugar cuts off the top of this curve when sugar is the precipitating agent. All quantitative data on pectin is specific for the samples used, because of the varying amounts of electrolytes in unpurified pectin.

The working hypothesis for this boundary line: Pectin sol is stabilized by adsorbed water and anions. The soluble organic compounds which destabilize the sol do so, first, by lowering the vapor pressure of the dispersion medium, and second, in some cases at least, by neutralizing the negative charge given by anion adsorption. Increased hydrogen or hydroxyl ions on either side of the maximum in the curve, decrease the amount of adsorbed water and so reduce the amount of precipitating agent required.

A jelly results if the precipitated pectin agglomerates to form a net-work structure strong enough, either because of its density and continuity or because of its rigidity, to support the weight of the mother liquor.

Acknowledgment

One discovery which each of Professor Bancroft's students makes, is the possibility of using chemistry as a vehicle of thought. Isolated facts as such lose their importance under his teaching and their value accrues only with their service in logically explaining cause and effect. Under Professor Bancroft's guidance research becomes truly a philosophy which reaches far beyond the laboratory. Fortunate and grateful are we who have had the privilege of working under his direction.

Thanks are due the Certo Corporation for the generous fellowship on which a part of this work was done.

The Department of Spectroscopy of Cornell University made and read the spectrographs of pectin ash and for this I wish to express my thanks.

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THE EFFECT OF SALTS ON SUGAR-PECTIN JELLY-FORMATION

BY GENE SPENCER

Salt Effect on Pectin Sol in the Absence of Sugar

The destabilization of pectin sols by soluble organic compounds has been described in the preceding paper.[1] Destabilization by inorganic salts is now to be considered.

Before considering the influence which added salts have on pectin sols containing sugar, we shall consider what has been observed as to their influence on a pectin sol in the absence of sugar.

Variable Factors in Precipitation

A review of the literature relating to salt action on pectin sol shows very little agreement as to the peptizing and precipitating action of different salts. These discrepancies are probably, in a large measure, traceable to the failure to recognize certain variable factors in manipulation.

Weiser[2] has outlined some of these factors which must not be overlooked in the precipitation studies for colloids in general. The variables which influence most the completeness and the form of a pectin precipitation are the temperature of precipitation, the rate and order of addition of constituents, the concentration of pectin, the other electrolytes present and the acidity or alkalinity of the dispersing medium.

Fremy[3] so long ago as 1840 pointed out another important variable. One of the most conspicuous properties of pectin is its precipitation by certain metallic salts. The early workers assumed this precipitate to be a pectate and Fremy, like many of the others, attempted to make and analyze these salts. He reported that the percent of lead in the compound which he had assumed to be lead pectate, varied with the treatment to which the pectin had been previously subjected. This original physical condition of pectin still holds as an important variable in studying its behavior with salts.

Concentration of pectin is very important and often overlooked. It is an experimental fact that one concentration of pectin will give a gelatinous precipitate with sodium sulphate, whereas a more dilute pectin sol will not. One would suppose that destabilization occurs in both cases, but is evident only in the one where it is accompanied by agglomeration due to higher pectin concentration.

As to the presence of other electrolytes, it goes without saying that when the influence of the impurities become too pronounced we lose sight of the influence of the variable and so we learn nothing.

It must be admitted that the salt effect on a pectin sol is a composite of many tendencies, some of which we recognize and understand, others which we do not understand, and still others, doubtless, which are not yet recognized. We shall assume that in general the qualitative facts of pectin precipitation by salts are determined by the summation peptizing effect of the anions present as against the summation precipitating effect of the cations present. But quantitative values are, as yet, representative of the peculiarities specific to the pectin used and to the experimental manipulation.

Influence of Bases in Salt Precipitation

Since the anions of base and acid both tend to stabilize pectin, the cations of either at sufficiently high concentrations should tend to neutralize the adsorbed anion charge.

Experimentally, metallic ions do precipitate pectin. This may be shown by treating a 1% pectin sol with a strong salt solution made alkaline with sodium hydroxide, when precipitation will take place at once.

An alkalinity is taken such that without the salt there will be no precipitation. There is then no question of the precipitate being a product of hydrolysis.

The theoretical explanation of this precipitation is that the summation peptizing influence of the adsorbed chloride and hydroxyl ions is exceeded by the summation destabilizing effect of the sodium ions of the base and the salt.

Haynes[4] has already made it clear that these combinations of alkali and salt which are able to precipitate pectin owe their power to the cation. She pointed out that the effect of the alkali "was increased by its salt which would depress ionization of the hydroxide and thus lower the concentration of the hydroxyl ion. This makes it appear that the positive rather than the negative ion is the effective agent."

Haynes found that a gel formed by an alkali hydroxide and its salt was reversible, but that an alkaline earth hydroxide with its salt gave an irreversible precipitate. We were unable to duplicate this last result but found that if the precipitating agent was washed out at once, the alkaline earth precipitate of pectin was also reversible. Bancroft[5] has treated the reversibility of colloid precipitations thus: "With a colloidal solution stabilized by an adsorbed ion, the reversibility of the coagulation depends upon the possibility of washing out the precipitating agent and on the physical state of the precipitate. The more strongly the precipitate is adsorbed the more difficult it will be to wash it out. When albumin is precipitated by sodium chloride, the coagulation is ordinarily reversible. When it is precipitated by the salt of a heavy metal, the coagulation is irreversible. All precipitates tend to change on standing, becoming coarser or more firmly agglomerated. It may then happen that washing out the precipitating agent will not cause peptization. When albumin is precipitated by calcium chloride, the coagulation is reversible if the calcium chloride is washed out at once; but is not reversible if the precipitate is allowed to stand. If a precipitate of silver chloride be allowed to stand overnight, it can then be filtered and washed much more satisfactorily than when first precipitated."

The aid which alkali gives to precipitation of pectin by salts is also noticeable with starch.

Bancroft[5] has summed up other instances of this cation effect in alkaline medium: "Colloidal silicic acid behaves like casein in one respect, that it adsorbs lime from suspended calcium carbonate. In accordance with this is the fact that silicic acid, though peptized by caustic soda and NH_4OH, is precipitated by barium hydroxide, because of the marked adsorption of the alkaline earth cation. It is also precipitated by alum and by basic dyes which is as it should be. On the other hand Mattson finds that the addition of caustic soda makes kaolin more sensitive to the precipitating action of calcium chloride in spite of the fact that hydroxyl ion peptizes quartz."

Influence of Acid on Salt Precipitation

On the acid side of neutrality it is a different story. Falk and McGuire[6] report that at a pH of 7, the alkaline earth salts gave a jelly formation under the conditions of their experiment, but that at a pH of 6, under the same conditions of precipitation, no precipitate resulted. von Fellenberg,[7] on the other hand, states that the chlorides of calcium, magnesium and barium gave no precipitates.

The disagreement between the results of Falk and von Fellenberg and also between von Fellenberg and our own observations with these salts is possibly due to differences in hydrogen ion concentration of the dispersing medium with which he worked.

Falk and McGuire[8] dialyzed a pectin sol against tap water and, when the pH was reduced to "7 or more," obtained a jelly. This is explainable on the basis of reduced hydrogen ion concentration together with the fact that dialysis had washed out the peptizing fruit acid ions and introduced less strongly adsorbed anions and more strongly precipitating cations.

The importance of acidity in salt precipitation of pectin sols is shown also by the fact that a sodium sulphate-pectin gel is peptized readily by hydrochloric acid; and, as Falk and McGuire have shown, that a calcium chloride concentration, which will cause precipitation in a sol of one acidity, may fail to do so in a sol of higher acidity. Increasing the salt concentration in certain cases will overcome the stabilizing action of the excess acid and cause precipitation, though in many cases, as for instance sodium chloride and hydrochloric acid, our pectin sol saturated with salt remains stable unless the sol is made alkaline.

Evidence that Pectin does not adsorb Hydrogen Ions readily

The stabilizing action of acids against precipitation by salts is the third evidence which we have had that hydrogen ions are less readily adsorbed than metallic ions. The other two were discussed in the first paper.

These three different experimental observations, (1) inability of acid to precipitate pectin under ordinary conditions, (2) persistent migration of pectin to the anode even in a strongly acid media, and (3) the stabilization of a sol against the precipitating action of salts, all point to the assumption of low hydrogen ion adsorption by pectin. From this evidence we must postulate that the peptizing tendency of acid anions in general is greater than the precipitating tendency of hydrogen ions.

Since an excess of alkali tends to aid pectin precipitation by salts, and an excess of acid tends to peptize pectin precipitated by salts as well as to prevent its precipitation by salts, the postulate is made that a gel-sol boundary curve for pectin is of the general form shown in Fig. 1. One should not lose sight of the very important fact that the quantitative value and even the trend of these gel-sol boundary curves for salt precipitation are specific not only for the manipulation and pectin sol but also for the acid and base used to adjust acidity.

This influence of acid on the precipitating action of salts may be an important factor in the extraction of pectin from plant pulp. When the pulp is made acid, the intersection point of the salt-hydrogen ion concentration falls in the sol region and the pectin forms a sol more readily.

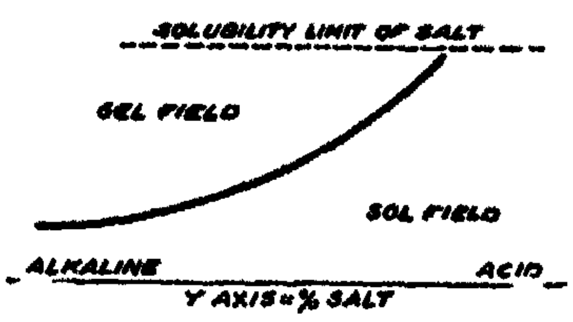

FIG. 1

A hypothetical boundary curve separating the gel-sol regions for pectin precipitated by salts.

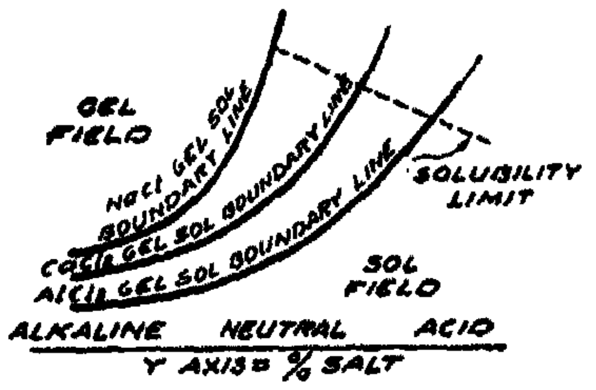

FIG. 2

Hypothetical curves designating the boundary line for the gel fields of the chlorides for three metals of different valence.

As previously stated the quantitative value of this curve would be specific for the pectin used and for the conditions of its determination, but the evidence is that with all pectin samples the boundary curve would have this tendency.

Influence of Preferential Adsorption on Relative Position of Boundary Curves

The relation of the gel field boundary curves for a series of salts having the same anion but different cations of the same periodic group is indicated by Falk.[6] He found that for his method the precipitating efficiency of the alkaline earth metals was in the order Ca> Sr> Ba. This is in harmony with Haynes'[4] observation that barium chloride gave no precipitate with pectin except on standing. According to this the calcium chloride gel-sol boundary line would be below the barium chloride line; that is, for the same condition of precipitation, more barium chloride would be required than calcium chloride.

Falk[6] found that sodium, lithium and magnesium salts did not give precipitation of pectin either above or below neutrality. This was our experimental observation in regard to sodium on the acid side, but as we have already described, an alkaline sodium chloride gave a precipitate with pectin.

Influence of Valence on the Relative Position of Boundary Curves

Extending Falk's[6] experiment to calcium and aluminum, we found that precipitation of pectin by aluminum was affected less by increased acidity, than precipitation by calcium chloride. On the alkaline side, the aid which increasing alkalinity gave to cation precipitating action was in the order Al > Ca > Na.

From these and similar experiments we postulate that the relation of these boundary lines will be found to be in accord with the order shown in Fig. 2.

The relative position of these curves for any given anion should by hypothesis be the same; for example, the sodium acetate curve should be above the aluminum acetate curve.

Influence of Preferential Anion Adsorption

A definite order of arrangement must obtain for the salts of any series having the same cation but different anions. Such evidence of anion adsorption as we have indicates that organic ions, especially those from fruit acids, are adsorbed more readily than inorganic ions. For these organic acid ions the order seems to be acetate >citrate> tartrate. That is, a sodium acetate gel-sol boundary curve would be above a tartrate boundary curve with the citrate curve between them. The evidence for this will be considered in connection with sugar jellies.

As to the inorganic anions, the chloride ions are adsorbed more strongly than the nitrate ions as is indicated by the fact that the negative charge of pectin has been reversed in cataphoresis experiments with nitric acid but not with hydrochloric, which would indicate a lower stabilizing power on the part of the nitrate ion. Sulphate ions also seem to be adsorbed less than chloride, since sodium sulphate but not sodium chloride will precipitate a 2% pectin solution in an acid medium.

There are so many factors which influence the precipitation of pectin by salts that this working hypothesis is set forth quite tentatively as a basis for further investigation of these influences. The hypothesis helps to explain salt influence on pectin jelly formation by sugar, as we have observed it, and it also helps to explain some of the records in the literature.

Salt Effect on Pectin Jelly Formation with Sugar

Ratner[9] has found that potassium ferricyanide may be substituted in whole or in part for sugar in pectin jelly formation. Halliday and Bailey[10] have found that a part of the sugar may be substituted by calcium chloride.

Halliday and Bailey do not state their observations in just this way but, in terms of our hypothesis of jelly formation by sugar, it means the same thing. They reported that the acidity could be decreased by adding calcium chloride. To the extent that calcium chloride may change either the real or the apparent hydrogen ion concentration of the dispersing medium, it is taking the place of the acid. But this effect on hydrogen ion concentration cannot be the whole story even though it may be part of it.

The sensitization of pectin so that it is more readily precipitated by sugar must be an important factor.

The empirical facts of the case in Halliday and Bailey's experiment seem to be that calcium chloride lowers the gel-sol boundary curve for sugar jellies; thus making the sol field smaller so that a lower concentration of acid or sugar or both will fall within the jelly field.

This also is probably the explanation for Ratner's results. The opposite is true for sodium chloride which, instead of lowering the gel-sol boundary curve on the acid side, raises it and so decreases the size of the jelly field making the sugar and acid requirement higher; and we say it hinders jelly formation.

The action of sodium chloride on the alkaline side of neutrality is quite different. In fact, in the case of every salt with which we worked, the sugar gel-sol boundary curve tended to be lowered on the alkaline side by the addition of salt. To sum up our observations graphically, the effect of salt on jelly formation is given in Fig. 3. To avoid the complication offered by the frustration of the sugar curve because of the solubility limit of sugar, the boundary curve of alcohol jellies is used.

FIG. 3

The qualitative gel-sol boundary line for alcohol jellies is given by the solid line. The dotted lines show the hypothetical elevation or lowering of this boundary line resulting from the addition of certain salts to the pectin sol.

Halliday and Bailey found that they could not substitute calcium chloride for acid indefinitely or a jelly too high in syneresis would be obtained. In terms of Fig. 3, as they moved the hydrogen ion concentration over toward neutrality, the amount of sugar required was increased. Instead of adding more sugar they added a second precipitating agent, namely, calcium chloride thus lowering the boundary line to meet the sugar concentration in the mixture. This they could not do indefinitely, however, and still retain the properties desirable in a sugar jelly, since they eventually tended to form a calcium chloride jelly rather than the sugar jelly normal for that acidity. Salt jellies are noticeably higher in syneresis than sugar jellies.

This difference in syneresis may be due to a difference in structure or, following McNair's[11] suggestion, to a difference in viscosity of the mother liquor, water being displaced from its adsorbed state without a concomitant increase in the sugar concentration of the mother liquor.

The sensitization of a colloid by one precipitating agent so that its precipitation may be completed by a second precipitating agent is well recognized. Gurchot[12] sensitized a sol of ferrocyanide by salts so that it was brought down by a few drops of alcohol. Wickmann and Chernoff[13] have reversed this for pectin. They found that 10 mg. of pectin dissolved in 220 cc. of water treated with a certain amount of alcohol did not give a precipitate but that the addition of electrolytes caused a pectin precipitate to form.

Importance of Salts in the Jelly-Forming Value of a Pectin Sol

There has been a tendency to attribute the jelly forming value of a given juice, or sol to the amount or kind of pectin which it contains, even though no adequate method of obtaining these data is available. Acidity has been given, more recently, due recognition, especially since the work of Goldthwaite[14] and Tarr.[15] The criterion for the value of a fruit juice in industry is the amount of dilution by sugar which the juice will permit and still give a satisfactory jelly; this rests on a purely empirical basis, because as just stated no quantitative pectin test has yet been found which will serve the purpose of standardizing the juices.

The point to be made in this connection is that salts have not been given due recognition either in the attempts at quantitative estimation of pectin or in its evaluation by the jelly forming power of the juice. It is a well-known fact that a relatively small amount of sodium chloride will make a good juice unfit for jelly making and, as Halliday and Bailey have shown, a small amount of calcium chloride will enhance the jelly-forming value of a juice.

The behavior of different salts is satisfactorily explained on the basis of the hypothesis that, because of the specific adsorption preference of pectin for their ions, some salts lower and others raise the gel sol boundary curve.

Many salts under certain concentrations and with certain acids or bases, appear simply to delay rather than to change the amount of acid or sugar required to give a jelly. Whether the precipitation formed after the delay would be identical with that formed without the addition of the retarding constituent cannot be stated. One could determine this by studying the jelly strength of cold-method sugar jellies formed with and without the addition of the salt in question.

The obvious explanation for a delay without weakening of jelly formation, is the displacing of one adsorbed ion by others of higher concentration or perhaps higher preferential value. The reaching of ionic equilibrium such as would take place for the same constituent in the absence of pectin, may also be a factor in this retarding influence of salts.

Acid Anion Effect on Pectin Jelly Formation

This brings us to the necessity of considering the anion of the acid with which we adjust the acidity in any series of sugar jelly formation. The more strongly adsorbed the anion is, the larger will be the sol field. Goldthwaite[14] found that tartaric acid was much superior to citric in jelly-making by the hot process and the work of Tarr,[15] and Myers and Baker[16] have substantiated her results.

The following data from Tarr incorporated in Table I is of interest:

TABLE I

	cc. 0.1 N Acid	pH	Jelly Strength Pressure cm. Water
Tartaric	10.0	3.19	60.5
Citric	20.0	3.18	46.5

In Goldthwaite's work the criterion of superiority of tartaric acid over citric acid, was "texture and flavor" of the product when the same amounts of acid were used. In Tarr's work, the criterion was the amount of acid used to yield an "optimum" jelly.

We do not believe that the difference in the amount of acid required to give a certain pH is of first importance, because of the uncertainty of salt impurities in the pectin used. It is significant, however, that at the same pH, the jellies are of such different strengths.

The fact that the citrate makes a weaker jelly indicates that there is greater citrate ion adsorption and so greater resistance to destabilization.

Myers and Baker have made a real contribution to this study as far as the practical applications are concerned. Their results are not entirely in accord with the development of this hypothesis, but the variations, we believe, are all explainable in terms of the unavoidable changes which take place as a result of the evaporation method which they used.

Conclusion

1. The stabilizing anion charge on pectin may be neutralized by cation adsorption either with or without the presence of organic precipitating agent.

2. Concentration of pectin and manipulation in combining constituents are important in salt studies. Acidity or alkalinity of the dispersing medium and the ions of the added acid and base are also very important factors. The cold method of jelly-making with several precipitating agents, is recommended.

3. Salts as a whole precipitate pectin more readily in alkaline than in acid media. It is postulated that the gel and sol regions for this precipitation may be separated by a definite boundary line. If the salt and acid (or alkali) concentrations intersect within this gel field, a precipitate will form. This precipitation may then be reversed by changing the salt-acid (or alkali) concentration relation to one within the sol region, as by washing out the precipitating salt or increasing the hydrogen ion concentration.

4. A given amount of salt will aid in the sugar precipitation of a given pectin sol if it lowers the sugar jelly boundary curve of that particular pectin sol. If it raises the boundary curve, it will hinder jelly formation, or at least retard it.

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NEW BOOKS

2

Salts, Acids, and Bases: Electrolytes: Stereochemistry. *By Paul Walden. 23 × 16 cm: pp. 397. New York and London: McGraw-Hill Book Company, 1929. Price: $4.00.* This book contains the lectures given by Professor Walden during the first term of 1927-1928 when he was the George F. Baker Non-Resident Lecturer in Chemistry at Cornell University. Part I deals with salts, acids, and bases; Part II with electrolytes and non-electrolytes; Part III with the electrical conductivity of non-aqueous solutions; and Part IV with stereochemistry and the Walden inversion.

"On the basis of what has been discussed, K. A. Hofmann defines acids and bases as follows. Laying particular stress on the lability of the acid hydrogen atom, he says that true acids are substances containing a labile, reactive, and replaceable hydrogen; true bases such as the alkalies, *e.g.* KOH, are substances with a labile hydroxyl group capable of forming salts with separation of water.

"This definition brings us to the end of a classical, century-long, period of development of the concept "Acid, Base and Salt," a development resulting chiefly from experimental investigations. This definition really contains all the essential, observable characteristics of these substances as they are met with by the organic and the inorganic chemist, and it is thus that they are regarded in present-day theory and research.

"At the same time by its qualifying term "true (Echt)" the definition points toward the new, modern, concept that takes account of new experimental facts and new theoretical foundations," p. 69.

"One often hears to-day the blunt statement—that theory is "wrong;" but no scientific view is "wrong" if it is based upon actual facts and is reached by logical reasoning. It may be incomplete. It may be based on insufficient data. It may later be refuted by newly ascertained facts, but nevertheless it was true for a given state of knowledge and it often happens that from a new standpoint or in a more advanced period of our science we return unconsciously to former so-called false views and, using new facts, we recreate theories that are analogous to the old. In our historical survey, reference has frequently been made to such cases of revival of forgotten scientific ideas; and many of the seemingly original theories of the present day can be traced back to the views of the earlier chemists. Indeed it would appear that the fundamental concepts concerning nature exhibit a law of conservation analogous to the law of conservation of energy.

"Furthermore, it is evident that all scientific ideas and theories must have a favorable "culture medium." This brings to mind an old French quotation concerning a famous man which reads as follows: "Il ne suffit pas d'être grand homme, il faut venir à propos." The same thought might well be applied to a theory. It is quite essential that it appear at the "right time," but it is a difficult matter to ascertain the exact psychological moment for its presentation. It was known in the year 1500 that burning metals increased in weight; Lemery knew in 1675 that the process of combustion was linked with the consumption of something that came from the air. Mayow (1674) knew that a special kind of matter existed in air and gave it the name "spiritus nitro-aërius." But not until 1780 did Lavoisier create his oxygen theory. Lavoisier presented his ideas at the proper time! The large collection of new facts and the inadequacy of the traditional views and explanations required the creation of a new idea.

"However, a third factor enters at this stage. A new idea needs followers, scientific apostles. It must find mental resonance. The great success of Lavoisier's theory was due not only to its scientific charm and simplicity, but also to the fact that it was accepted by the younger chemists in all countries. The "culture medium" for Liebig's hydrogen theory of acids was certainly his famous chemical laboratory at Giessen. His laboratory was indeed a world laboratory. It attracted students of chemistry from all civilized countries. One could hardly say that the success of Arrhenius' theory of electrolytic dissociation lay in the fact that it was the brain-child of a brilliant physicist. It was the laboratory of chemistry of Wilhelm Ostwald which helped to spread his doctrine—a laboratory which was then to modern physical chemistry what Liebig's was to organic chemistry fifty years previous. Ostwald's laboratory was a great collector of mental energy, for to it came the young and talented chemists from all over the world to embrace and become followers of new ideas and methods. Indeed, Ostwald himself was a most clever and indefatigable interpreter and promoter of this theory of Arrhenius, and by his unique and exceptional personality made many scientific converts," p. 71.

"In 1879 "Kohlrausch leaves it an open question whether hydrogen chloride is present in solution as HCl, or $HCl.H_2O$, or $HCl.2H_2O$. He does not support the general theory that ammonia is present in water as NH_4OH, since its behavior as an electrolyte contradicts this idea. Its conductivity curve is very different from that of strong bases. It must, therefore be present as NH_3 and act as a conductor," p. 114.

"There exist also metallic hydroxides, such as $Zn(OH)_2$ and $Al(OH)_3$, which can add on both hydrogen and hydroxyl ions and form salts. These are known as amphoteric hydroxides and will be discussed later as amphoteric electrolytes," p. 120.

"This theory of two isomeric forms of acids, viz., pseudo-acid$\rightleftarrows$true acid, is not accepted by Fajans who justly contends that the optical differences which have been used as the basis for the existence of such an isomerism, may very well be explained and even necessitated by the process of dissociation. The observations of H. Ley and Hünecke are also of importance in passing judgment on this question. These investigators made optical absorption measurements in the ultra-violet on certain carboxylic acids, their esters, and their salts, and state that "there is absolutely no reason why we should assume that the solvent effects noted in the case of these acids should be explained by rearrangement (acid$\rightleftarrows$pseudo-acid)." Even esters which are incapable of rearrangement show no optical constancy and are influenced by solvents to as great an extent as the acids themselves. "The change in the spectrum of the carboxylic acids wrought by salt formation is of a magnitude equal to that called forth by the solvents." Ley, von Halban, and Fajans, explain these changes in dissociating acids by the deformation of the outer shell of electrons of the acid anion produced by the approach of the hydrogen nucleus. Interesting, also, is the statement by Ley that the ability of the ester group, COOR, to solvate might well be expected to be different from that of the carboxyl group, COOH. He also suggests that it is not the whole dissolved molecule which is entirely surrounded by solvent molecules, but that the latter are attached only to certain 'lyophile' groups," p. 128.

"Truly, one cannot deny the sagacity and the interesting mental processes which permit us to call potassium chloride or sodium chloride 'bases,' when these typical salts are dissolved in hydrogen chloride; one is also at liberty to call aluminum chloride an acid, when the latter is dissolved in phosgene and eventually forms a complex compound. But on the other hand, one may justly inquire whether there is any practical necessity for such a course of action, whether it represents an advance when *scientific names*, established as the result of experiment and based on definite theoretical considerations, are taken as marks of distinction for phenomena which differ, although they are formally singular. Is there any advantage in such a procedure? Does it not portend a degeneration of our scientific concepts and terms? Would it not be better in place of the more or less sweeping generalizations, to retain the old established names and concepts with their hydrogen and hydroxyl ions based upon the behavior of aqueous or water-like electrolytic solutions, and to introduce *special* terms for the exceptional cases dealing with new types of solvents? Let us not forget the application of the old classical definitions to analytical, technical, physiological chemistry and biochemical science," p. 158.

"Hückel arrives at his theory of strong electrolytes in the following manner. "Let us assume that there exist completely dissociated electrolytes and let us calculate, theoretically, how these should act. One ascertains that there are electrolytes which behave in accordance with such deduced properties. These will now be assumed to be wholly dissociated. These are the electrolytes which have been designated as strong." It is evident that this definition has been worded very carefully. No references to the constitution of electrolytes, no dependence upon the type, no general prediction as to their strength are given. It therefore becomes necessary to determine separately for each individual electrolyte whether or not *it is to be called a strong* electrolyte," p. 181.

"In general, the dissociation constant, K_z of typical binary salts should be about $K = 0.022$. This value is in fair agreement with the one obtained by Weiland for potassium chloride, $K = 0.020$. A value $K = 0.0211$ was obtained by Bencowitz and Renshaw for *trimethyl sulphonium* iodide, $S(CH_3)_3I$, at 25° at dilutions $v = 11000$ to 100000, while the dissociation constant $K = 0.0252$ was obtained for tri-ethyl sulphonium bromide at dilutions $v = 12000$ to 100000. In general, a constant K value is obtained in the case of these three binary salts where the degree of dissociation is above $\alpha = 0.996$ and the dilution, v above 11000-14000.

"We may therefore consider it an established fact that the typical binary salts (halides) which have been examined, obey the mass law in aqueous solutions at dilutions above $v = 10000$-14000," p. 186.

Bjerrum says: "The typical strong electrolyte is one composed of rigid, unchangeable ions. As worked out in the last few years, the trend of the theoretical views *on strong* electrolytes has been such as to attempt to explain all properties of electrolytes by aid of interionic forces on the basis of the unchangeability of the ions. . . . In accordance with the most recent views those electrolytes are designated as strong whose ions do not combine measurably with one another under *observed conditions*. Since the ions of strong electrolytes do not, in general, mutually deform each other, it seems logical to regard as the ideal strong electrolyte that substance composed of non-deformable ions," p. 192.

"The square-root formula is valid for all solvents investigated thus far, but its application is dependent upon the dielectric constant ϵ of the solvent. The smaller the value for ϵ, the higher will be the dilution range at which the λ, v-curve will begin to approximate a straight line. The calculated values for $v = (270/\epsilon)^3$ given in the last column of the above table show a satisfactory agreement with the v-values at which the square-root formula becomes valid. The empirical equation $v = (270/\epsilon)^3$ offers a means for predicting this characteristic dilution, provided tetraethyl- or tetrapropylammonium picrates are employed. Applying this equation to benzene and chloroform the following results are obtained:

Chloroform: $v = (270/4.95)^3 = 162000$ liters
Benzene: $v = (270/2.19)^3 = 1870000$ liters.

"In other words the square-root formula for strong binary salts would become valid in these solvents at dilutions $v \sim 20000$ and 2000000 liters respectively," p. 214.

"On the basis of conductivity data that have long been known and repeatedly verified, it is generally assumed that the alkali halides—for instance, those of sodium, potassium, and lithium—are typical binary salts which are similar in behavior and dissociated to practically the same degree in water and alcohols. It has furthermore been assumed as true that salts made up of univalent radicals, such as the ammonium and alkylated ammonium bases, may be considered as typical binary salts which, like the alkali halides, "are dissociated to nearly equal extent in equivalent solutions." Direct conductivity measurements in methyl and ethyl alcohol and water have verified this view.

"However, in acetone solution conductivity measurements show that there has been a separation of these salts, previously considered similar and equally dissociated. They have divided into one group of 'normal,' strong, or typical binary salts—the tetra-alkylated ammonium compounds—and several sub-groups of moderately strong to extremely weak, poorly conducting salts. These studies have revealed furthermore, that the conductivity values in each of these sub-groups shows a decided dependence on the nature of the halogen ion. This influence upon conductivity and upon dissociation—expressed by $\alpha = \lambda_v/\lambda_\infty$—can be illustrated by the following series. Anions: picrate > iodide > thiocyanate > bromide > chloride. (The triamylamine salts of picric and thiocyanic acids have also been included.) It has definitely been shown that these extremely low conductivity values are not caused by solvolysis," p. 242.

"The Kohlrausch law has been tested with reference to its applicability to the equivalent conductivities λ_∞, calculated for definite dilutions, $v = \infty$, by means of the square-root formula. It has been found to hold:

(1) in aqueous solutions up to 100°, as well as in non-aqueous solutions between $t = -33.5$ to $+50°$,

(2) for both elementary univalent cations and anions, as well as for large univalent organic ions,

(3) for both non-aqueous solvents with high di-electric constants and pronounced dipolar character such as the alcohols and ammonia, as well as for the so-called non-conductors, the halogen hydrocarbons, as ethylene chloride with $\epsilon - \leqq 10$," p. 283

"Employing one and the same electrolyte, $N(C_2H_4)_4I$, in non-aqueous organic solvents, the *product of the internal friction and the limiting conductivity, $\eta.\lambda_\infty$, is independent of the solvent and of the temperature.*

"The $\lambda_\infty.\eta = K$ rule was received like so many other new theoretical pronouncements. One group of scientists ultimately regarded it as a perfectly obvious generalization which had long been known, and linked it with Stokes' law. The other group discarded it as faulty and inadequate.

"It is to be assumed that the previously mentioned specialists (Jahn, Abegg, and others) knew of the Stokes law (1850) dealing with the slow stationary movement of a sphere in a liquid. Nevertheless, they stated that not even a theoretical relationship between the mobility of the ions and the properties of a medium could be predicted. Later, Stokes' law

$$K = \text{constant} = 6\pi.\eta.r.v.$$

(where v = velocity, η viscosity, r = radius of the sphere) was repeatedly applied to ions and their mobility as dependent on viscosity.

"In particular by the comprehensive measurements of Dutoit and Duperthuis using sodium iodide in ethyl, propyl, isobutyl and amyl alcohols, as well as acetone and pyridine, was the Walden rule $\lambda_\infty.\eta = K$ shown to be apparently not verifiable. No constant for the product $\lambda_\infty.\eta$ could be obtained either in one and the same solvent at different temperatures, or in various media at the same temperature," p. 286.

"In water the ion mobilities of the three cations [potassium, sodium, and lithium] differ widely from one another. These differences are considerably smaller in ethyl alcohol, the relationship being approximately the same in both ethyl and methyl alcohol. In acetone the mobilities have become practically identical. If one assumes that this gradual equalization of these ion mobilities depends upon an adjustment of their ionic radii due to decreasing solvation of the Li^+ ions, it is justifiably conceivable that the solvation of the Li^+ and Na^+ ions, respectively, may be decreased to such an extent in certain solvents that the order of mobilities may become completely reversed and

$$Li^+ > Na^+ > K^+$$

Examination of the measurements of Morgan and Lammert in acetophenone with this idea in mind supports this assumption," p. 318.

"Use of various solvents eventually differentiates these two substances, diethyl ammonium chloride and tetraethyl ammonium chloride which we recognize as being of equal strength in aqueous solution. The first retains the characteristics of a strong salt, while the other gradually becomes weaker and weaker, finally to be classed as a non-electrolyte in ethylene chloride. The concept 'strong salt,' in so far as it has been deduced from conductimetric behavior in aqueous solutions, must be qualified by a statement of the chemical nature of solute and solvent. Just as the hydrogen salts, that is, acids, may grade. from strong to weak electrolytes or to all intents and purposes become non-electrolytes, according to the nature of the solvent, so also may the alkylated ammonium salts, as well as the lithium and silver and other salts, vary in behavior depending upon the medium in which they are dissolved. Solvents may also effect a differentiation of the ions themselves. When combined with one and the same *cation* in aqueous solutions, the halide, nitrate, and chlorate ions exert a dissociation effect which is practically the same. This effect is shifted to an appreciable degree in non-aqueous solvents, and salts formerly of equal dissociating power become of different strengths, assuming the following relative positions: chloride $<$ bromide $<$ nitrate $<$ iodide $<$ perchlorate $<$ picrate. These findings make it possible to synthesize electrolytes or salts of varied 'strength.' It can be shown in this manner that salts of the best conducting type, that is those composed of a tetra-alkylated ammonium cation and of a picrate, perchlorate or iodide anion, give electrolytically conducting solutions even in the so-called 'non-conductor' benzene.

"On the basis of measurements presented, the rôle of the solvent in the conduction of a dissolved salt does not appear to be altogether simple. The selective solubility of salts, color changes, and formation of solvates, seem to point to 'chemical' relationships between solvent and solute. So far as physical properties of the solvents are concerned, it has been established that the dielectric constant, ϵ, and the viscosity, η, exert a very definite influence upon the "degree of dissociation" (i.e. $\alpha = \lambda_v/\lambda_\infty$) and the numerical size of the conductivity, respectively," p.322.

In regard to the Walden inversion Walden quotes, p. 355, from Stewart: "In the whole field of stereochemistry, no more puzzling phenomena are known than those grouped under the head of the Walden Inversion, and at the present day we still await a solution of the problem. The data are so complicated that it would be impossible to deal with them fully here."

"Up to the present time no less than twenty-five theories have been advanced to explain this phenomenon. The discoverer of this inversion has had the unusual honor of seeing the most influential men gathered around his "brain child." They have bestowed gifts upon this child, and many of them have proposed chemical or physical theories to explain the nature of this phenomenon. Although in the meantime this child has grown up, and has reached the age of thirty years, chemists who are studying the configuration of molecules still regard it as an *enfant terrible.* Although many suggestions have been advanced to explain the phenomena grouped under the 'Walden Inversion,' a completely satisfactory solution has not yet been attained nor has it been found possible to predict the course of an inversion," p. 384.

Wilder D. Bancroft

Molecular Physics and the Electrical Theory of Matter. *By J. A. Crowther. Fourth edition. 19 × 13 cm; pp. viii + 202. Philadelphia: P. Blakiston's Son and Co., 1927. Price: $2.50.* In the preface the author says: "The progress of Science is, nowadays, a generally accepted commonplace, but no one can be more acutely aware of how rapid this progress is than the author of a volume such as the present, who finds himself faced, from time to time, with the pleasant but by no means easy duty of attempting to keep his book abreast of the modern developments of his subject. In no part of physics has the advance been more rapid than in the investigation of the properties and structure of the atom. New experimental methods have enabled us to sound the depths of the atom and to map out its levels with the certainty of an oceanographical survey. Sir Ernest Rutherford and his students are already battering down the defences of its innermost citadel, the nucleus, with their atomic projectiles, while the work of Bohr and other quantum mechanicians is giving a theoretical basis for the experimental observations.

"As these developments were foreshadowed in the previous edition they have involved an extension rather than revision of the text. To make room for so much additional material without unduly increasing the size of the book I have been compelled reluctantly to abbreviate the accounts of the earlier theories of atomic structure; reluctantly, because the methods by which science advances are as interesting and as valuable as the results which it achieves. I have tried to preserve sufficient of the original material to illustrate the historical development of the subject."

The chapters are entitled: introduction; the physics of the electron; the positive particle; positive ray analysis; the nature and size of an electron; the structure of the atom; the electron in chemistry; the atom in vibration; quanta and electrons; the molecular theory of matter; the atom in dissolution.

There is an interesting foot-note on p. 13. "The science of electricity is burdened with two distinct systems of units for the measurement of electrical magnitudes, the one founded on the consideration of the force with which two similar charges repel each other, the other on considerations of the induction of currents by magnets. The practical system of units is founded upon the latter, the volt being 10^8 and the ohm 10^9 absolute electro-magnetic units. The ampere and coulomb are thus one-tenth of the absolute units of currents and charge. To make confusion worse confounded, it has become usual in books and original papers on these subjects to give the value of m/e in electro-magnetic units, while the value of e itself is usually given in electro-static units. Our statement that the force on the electron due to the magnetic field is equal to H.*e.v.* implies that we are using the absolute electro-magnetic system of units, as this system has been defined in such a way as to make this statement true. As this system is the one more closely related to the units in practical use, we shall employ it throughout, except where the contrary is explicitly stated."

The method of positive ray analysis "enables us to detect with certainty the presence in a gaseous mixture of far smaller quantities of an element than could be accomplished by any other method known to science. . . . The new method has the further advantage over spectroscopic analysis that it gives directly the atomic or molecular weight of the substance under experiment. . . . Lastly—and this is perhaps most important of all from the point of view of an intimate study of the modes and methods of chemical combination and decomposition—the time taken for each single particle to register its presence and mass is exceedingly minute. A very moderate value for the speed of the positive particles is 10^8 cms. per second (about 620 miles per second). Their path in the discharge tube is not more than 50 cms. in all. Thus a particle when caught by the discharge will register itself on the photographic plate in considerably less than one-millionth of a second.

"We might therefore reasonably expect to find on the photographs curves corresponding to temporary combinations of atoms so unstable that their whole period of existence is not greater than one-millionth of a second, of any such combinations are formed in the discharge tube. Thus in the case of chemical reactions taking place within the discharge tube we might expect to find on the plate traces not merely of the stable products of the reaction but also of any intermediate stages occurring in the course of the reaction. The field thus opened up for an intimate study of the mechanism of chemical reactions is illimitable.

"Though little has as yet been accomplished along these lines, the experiments already made show that this expectation is not unfounded. As a very simple illustration of the application of the method we may take the case of phosgene, $COCl_2$. When this was introduced into the apparatus the photographs showed that, in addition to the molecules of undecomposed phosgene (99), the carriers of positive electricity were molecules of carbon monoxide (28) and atoms of chlorine (35.5). The lines due to single atoms of carbon and oxygen were very faint indeed, thus showing that the decomposition of the compound by the discharge consisted of the separation of the chlorine atoms from the CO molecule, the bond between the carbon and oxygen atoms remaining intact.

"This is a simple case where the results obtained might easily have been predicted. Another interesting case is that of methane, CH_4. When this gas is subjected to the discharge a group of five lines appears on the photographic plate, indicating the presence of particles having masses 12, 13, 14, 15 and 16 times that of the hydrogen atom. These correspond to particles having the composition C, CH, CH_2, CH_3, and CH_4 respectively," p. 55.

"In the realm of science an insufficient, or even a false, hypothesis is better than none at all, and it will be useful to take the best approximation we can devise to serve us as a clue through the labyrinth of experimental facts which we have still to consider. At the same time it will be well to point out carefully where we are treading the solid ground of experimental fact and legitimate deduction, and where we rise to the higher but more precarious flights of scientific imagination," p. 61.

"We are thus led to divide chemical compounds into two great classes: those in which the forces between the atoms have not been sufficient to bring about the passage of an electron from the one to the other, and those in which such an exchange has taken place.

Molecules of the second class may conveniently be termed '*ionized*,' and the process may be spoken of as *intra-molecular ionisation*. In the former class we should naturally place molecules such as H_2, O_2, CO, NO, etc., the constituent atoms of which do not differ very widely in their electro-chemical character; to the second or ionised class we should assign compounds of the more violently opposed elements, such as H_2O, H.Cl, NH_3, together with the whole class of electrolytes. These results are borne out by the experiments with the discharge tube," p. 112.

"On the other hand, if the two charges of the doublet are situated on different atoms, the setting of the doublet will necessitate the rotation of the whole massive molecule—obviously a much slower process. Now in the case of ordinary electrical experiments, where the field is usually applied to the substance in the same direction for at least an appreciable fraction of a second, there will be ample time for these heavy doublets to adjust themselves to the field, and they will thus add their full value to the specific inductive capacity of the substance. In the case of such very rapid oscillations of the field as are known to occur in waves of light this adjustment will obviously be impossible, and the specific inductive capacity as deduced from optical experiments will be much less than that obtained from electrical experiments of the usual kind.

"Now, Maxwell has shown that on the electro-magnetic theory of light there is a simple relation between K, the specific inductive capacity of a substance, and n, its refractive index, which may be expressed by the equation $K = n^2$. It is well known that in many cases the value of K deduced from this expression is identical with that obtained by direct electrical measurement, but that in others the relation does not hold even approximately. For example in the case of water, electrical measurements of the specific inductive capacity give a value of about 79, while that deduced from its refractive index by Maxwell's law is only 1.78. This discrepancy between experiment and theory has always been felt to be distinctly unsatisfactory, and science is indebted to Sir J. J. Thomson for this simple, adequate, and elegant explanation. It is an interesting confirmation of the theory that these discrepancies are always to be found in the case of compounds in which we know from independent evidence that the atoms are charged.

"We may therefore use the law of Maxwell as a means of determining to which of our two great classes of compounds any given substance belongs. If Maxwell's law holds, as in the case of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide, to mention only a few, the atoms in the molecule are uncharged. If, on the other hand, Maxwell's law does not hold, as is the case for water, the alcohols, ammonia, hydrochloric acid, etc., the compounds belong to the second class, and have intramolecular ionisation. It is obvious that the recognition of these facts will have important bearings in many directions. At present, however, we are only concerned with their application to the subject of valency and the nature of chemical affinity," p. 114.

"Michael Faraday, with almost uncanny prescience, seems to have felt that the relation between magnetism and light must be the closest, and sought for it with unremitting diligence. It is one of the little ironies of life that the only effect which he did discover (the magnetic rotation of the plane of polarisation) was one of the very few phenomena which theory even now is hardly adequate to explain. The effect he sought for was not discovered until, more than thirty years later, his experiments were repeated with stronger magnetic fields and far more powerful methods of spectrum analysis by Zeeman," p. 126.

"To solve the riddle, Professor Sir J. J. Thomson has hazarded the bold, but almost certainly correct, conjecture that the lines in the spectrum of hydrogen and, indeed, of many other elements are not emitted by the atoms of the element at all, but by systems which only exist when the gas is thrown into a luminous condition. When we consider the absolute identity of the spectrum of an element whether situated on the earth or away on the furthest star of which we have spectroscopic data, this hypothesis may seem to be the most startling we have yet advanced. It is, however, not without a very considerable experimental basis," p. 133.

"It is useless at present to speculate as to the mechanism by which this peculiar result is brought about. The merit of Planck's theory is not so much that it removes our troubles altogether, but that it packs them all together into one bag, so to speak, so that they become easier to handle. For the rest we can only regard the matter as a child regards an automatic machine, content with the empirical knowledge that a penny inserted in the machine will permit the extraction of a bar of chocolate, and that two half-pennies, though commercially equivalent, will produce no chocolate whatsoever," p. 143.

"Let us return now for a brief space to our solid again. Solids may be divided into two classes, according as they do or do not conduct electricity. It is also found that conductors of electricity are also good conductors of heat, while electrical insulators are generally very poor conductors of heat. We have by now come to connect electricity with electrons, and hence an electric current is a flow of electrons from a place of high to a place of low potential. We may regard a conductor, then, as a substance containing electrons which are free to move under the action of an electric field, while in non-conductors the electrons are fixed and unable to follow the impulse of the field.

"How are these electrons set free? In the first place it may be noticed that the only good conductors of electricity are metallic; that is to say, electro-positive in character, substances which we know from other phenomena readily part with an electron under slight provocation. Now in a solid such provocation may well be supplied by the close propinquity of the neighbouring molecules. It is well known that a charged body will attract uncharged substances. The attraction of a well-rubbed stick of sealing-wax for small pieces of paper is generally our first introduction to the science of electricity. The attraction is, of course, mutual, the force on the charged body being equal to that on the uncharged paper. Hence an electron in one atom is attracted by a neighbouring uncharged atom, and under favourable circumstances, and especially in the case of an atom only too ready to part with its electrons, the attraction may well be sufficient to enable it to make its escape.

"That some such assistance is necessary and is so given is shown by the fact that a metallic vapour is no better a conductor than any other gas at the same temperature. Thus while liquid mercury at its boiling-point is an excellent conductor of electricity, the mercury vapour above it conducts little better than the air it displaces—that is, practically not at all," p. 170.

Wilder D. Bancroft

The Collected Works of J. Willard Gibbs. *Edited by William Raymond Longley and Ralph Gibbs Van Name. Vol. I. 25 × 16 cm; pp. xxviii + 434; Vol. II, pp. xviii + 284. New York and London: Longmans, Green and Co., 1928. Price: $6.00 per set.* The 1906 edition has been exhausted, Lash Miller and his students having been the chief purchasers. As an introductory note to the present edition the editors say:—"The former edition of Willard Gibbs's writings, published in 1906 under the title *The Scientific Papers of J. Willard Gibbs*, did not include his important treatise *Elementary Principles in Statistical Mechanics* which had originally been published as a separate book and was at that time still available. In the present reprint this work has been included as Part One of Volume II, and this is therefore the first complete edition of the author's published writings. Permission to reprint the *Statistical Mechanics* was kindly granted by Yale University, holder of the copyright, a courtesy which is hereby gratefully acknowledged.

"There is no doubt that interest in the works of Willard Gibbs and appreciation of their fundamental importance have greatly increased in the twenty-two years since the publication of the former edition. It is hoped that this new reprint may serve to make the original text of his writings accessible to a far wider circle of readers than heretofore, and with this object in view the two volumes are offered at a low price. This has been made possible by the generosity of Professor Irving Fisher of Yale University, a former pupil of Willard Gibbs, and by the economy resulting from the use of photographic reproduction, which was also desirable as a means of avoiding typographical errors. The photographic method accounts for the slight typographical dissimilarity between Parts One and Two of Volume II, and for the separate pagination of the two parts, which on account of the footnotes could not readily be changed.

"As a supplement to this reprint of the original text, a commentary designed to aid the student of Willard Gibbs's writings may, it is hoped, be published at a later date. This volume, or volumes, to be written by recognized authorities in the several fields, would aim to explain the theoretical background of Gibbs's method, to amplify the treatment of points of special difficulty, to discuss the evaluation of Gibbs's functions in terms of directly measurable quantities, and to furnish a variety of illustrative examples from the literature now available. Such treatment is probably most needed in the case of the thermodynamic papers, but other parts of his writings may also be covered if it seems desirable. A special committee is now investigating the practicability of the whole plan."

The reviewer welcomes the statement that " a commentary designed to aid the student of Willard Gibbs's writings may, it is hoped, be published at a later date." Such a work will be invaluable if it is done really well and will be a great help any way. The anonymous reviewer in Nature said, among other things:—

"It is well known that Gibbs's work did not meet with great appreciation for many years, and after reading his papers it is interesting to consider why. We can imagine some elder of the Connecticut Academy after one of their meetings telling him as delicately as possible that he could not understand what the "Heterogeneous Equilibria" was about; and then Gibbs would go home and amplify it, expecting thereby to make it as clear to others as to himself. The result is that, once the chief idea is grasped, the whole is discussed in such great detail that it could scarcely be improved in ease or clearness. The whole trouble is at the beginning, and depends on the reader being able to feel the meaning of

$$d\epsilon \geqq t d\eta - p dv - \mu_1 dm_1 - \mu_2 dm_2$$

(Gibbs always considers the case of inequality with care), and for most of us it is unfortunately a considerable step from admitting the logic of the equation to the intuitive understanding of it. It is hard to see how amplifying his introduction would have helped; what is needed is habit of thought, and this can only grow with the lapse of time. His first paper on thermodynamics was published in 1873, two years before the great paper, and the right answer to anyone who complains about the "Heterogeneous Equilibria" is to advise him to spend, like Gibbs, two years over its preliminaries."

This may be true; but is it? We shall know when the proposed commentary comes out, because the author or authors will have to show that he or they understand Gibbs. It is open to anybody to imply, as does the reviewer in Nature, that he really understands Gibbs; but can he pass an elementary examination? Lash Miller and Donnan are probably the best two experts in the world on the subject of Gibbs; but neither one of them has ever published the equation for the change of the chemical potential with the concentration in a simple binary solution. Nobody has ever made an attempt to deduce reaction velocity equations for gases from the concept of the chemical potential. The usual answer is that thermodynamics has nothing to do with reaction velocity. This is true but not adequate. Guldberg and Waage deduced the mass law and the reaction velocity equations from kinetic theory. Gibbs deduced the mass law from the concept of the chemical potential. He stopped there, which was perfectly proper under the circumstances; but, when Gibbs stops, we stop. This may be a proof that somebody really understands Gibbs; but it does not look like it. All these things will have to be discussed in the proposed commentary, which should be an epoch-making volume. It may turn out that the words of Hafiz still apply to Gibbs.

To find the meanings that my lines bestow,
Waste not your wit, nor say: It's thus and so.
This pen you need not hope to understand—
Not even I will all its secrets know.

Wilder D. Bancroft

Crystal Structure and Chemical Constitution. *A General Discussion held by The Faraday Society, March 1929. 25 × 16 cm; pp. 253-420 + viii. London: Gurney and Jackson, 1929. Price: 8 shillings, 6 pence.* "The varieties of all things depend upon the varieties of their atoms, in number, size, and aggregation." So wrote Democritus well over two thousand years ago. One cannot avoid comparing this statement with the opening remark of Professor Goldschmidt in the volume now under review. "The task of crystal chemistry is to find systematic relationships between chemical composition and physical properties of crystalline substances, especially to find how crystal structure, the arrangement of atoms in crystals depends on chemical composition." And again, a little further on: "The structure of a crystal is determined by the ratio of numbers, the ratio of sizes, and the properties of polarization of the atoms." Changelessness is not usually considered an attribute of systems of natural philosophy. Yet it is possible to say that in crystallochemistry at least the hypothesis of the ancients has become a reality in our time; a reality that is, in the sense that, X-rays having provided the needful data for the elucidation of structure, it is possible to correlate atomic environment with chemical constitution.

The Faraday Society's Report of the Discussion held in London last March is essentially a collection of contributions by workers competent to add original knowledge, as well as criticism, to the general problem of crystal structure and its bearing upon chemical composition.

Professor Goldschmidt in his inaugural address shows how powerful the process of chemical substitution can be in tracing causal relationships between atomic environment in the crystal lattice, and properties of the substance as a whole. Thus for example: Why has magnesium fluoride the structure of rutile, whereas strontium fluoride crystallizes like fluorite? The answer is that Nature does not weigh the appropriate "bricks", she arranges them according to the space they require, and with regard to the amount of distortion which they inflict upon one another in the lattice. It is the ratio of the atomic radii of the constituents of a crystalline compound which—in the simplest cases—determines the resulting structure. When however, the atoms or ions are highly deformable under the influence of the intense electric fields existing within a crystal (especially when the corresponding forces are not directed symmetrically), then it is this property of polarization which is paramount, and the ratio of the radii diminishes in importance. Frequently however, both effects occur simultaneously. Rock salt is a substance almost entirely dependent upon ionic volumes for its structure, whereas solid carbon dioxide for example owes its molecular lattice—in which the units are CO_2—to the negligible deformability of carbon compared with the relatively high value for oxygen. There is little doubt that, on these broad principles, Professor Goldschmidt has gone far towards building up an adequate system of Inorganic Chemistry, free from the reproach of bordering upon the semi-empirical.

Papers to the General Discussion itself and grouped into four classes: (1) Inorganic, (2) Organic, (3) Metals, and (4) General. The subjects considered include sylvine, the silicates, ultramarines, the benzene ring, the metallic state, alloys, and a number of experimental matters, dealing for the most part with X-ray researches.

Professor Ewald has placed his readers under a debt of gratitude for his masterly sketch of the new wave mechanics, and their importance for our understanding of crystal structure. The resonance phenomenon, the Heitler-London application of the Exchange Principle and the Pauli "Verbot" are all helping to make history in the search for the mechanism underlying the stability of the crystal lattice.

This, the reviewer is aware, is not a comprehensive and accurately balanced account of the contents of this volume. It is a sheer impossibility to do the papers justice within the compass of a short notice: the best than can be done is to bring to the notice of physical chemists the chief points of interest to them, in the hopes that they will come to look upon this Report as one of the products by which the year 1929 will be remembered.

F. Ian G. Rawlins

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NAME INDEX

To Papers

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS · ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

NAME INDEX

To New Books

SUBJECT INDEX

Exclusive of New Books

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