Anonyme. The Journal of physical chemistry. Published at Cornell university [puis Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1934 . June-dec..

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Journal of physical chemistry

Tome 38

Volume 48

Washington 1934

RESEARCHES UPON PROSPECTIVE STANDARD SUBSTANCES FOR BOMB CALORIMETRY. VI

A Study of Succinic Acid

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Received August 18, 1933

I. INTRODUCTION

At a recent meeting, the Commission Permanente de Thermochimie (set up by the International Union of Chemistry) has adopted the principle of a secondary standard for bomb calorimetry and requested two of their number to investigate succinic and adipic acids, both of which appeared to be worthy of consideration as prospective secondary standards.

The present paper is an answer to the Commission's request in so far as succinic acid is concerned.

II. PREPARATION OF PURE SAMPLES OF SUCCINIC ACID; MISCELLANEOUS TESTS FOR PURITY AND STABILITY; PRELIMINARY COMBUSTIONS

Succinic acid, sold by the British Drug Houses (B.D.H.) as an analytical reagent guaranteed to satisfy their special standards of purity,[1] was used as the starting material. This was first recrystallized from conductivity water at a temperature kept below 70°C., in order to avoid the risk of some slight decomposition of the acid through loss of carbon dioxide which may possibly take place at higher temperatures.[2] The crystals were filtered through a Buchner funnel and partially dried by passing a current of air through them for several hours. After standing between filter paper for two days, the acid was well crushed (in small portions at a time) in a mortar; it was then spread in thin layers in large Petri dishes and

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[1] For some details, see section III, paragraph 1.

[2] According to Lamouroux (4), saturated solutions of either oxalic or malonic acids give rise to very large bubbles of carbon dioxide (with simultaneous formation of acetic acid) when heated to 68°C.; similar decompositions may possibly take place with saturated solutions of the homologues of the above acids, though this was not actually observed by Lamouroux, perhaps merely because it was not sufficiently apparent.

To get the acid quickly into solution without having to raise the temperature above 70°C., nearly four times as much water as would have been required at 100°C. was used. The solubility of succinic acid is 1 per 0.81 part of water at 100°C., and 1 per 19 parts of water at 15°C.

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dried for two further periods of 6 hours (each of these being followed by careful crushing), in a desiccator containing fresh phosphoric anhydride, under a pressure reduced to approximately 0.1 mm. of mercury.

Two portions of about 4 g. each were now introduced in two weighing bottles and left to stand over phosphoric anhydride in an evacuated desiccator, the loss in weight being recorded from time to time so as to ascertain to what extent the drying had been carried out. The results given in table 1 were obtained. The loss in weight recorded during the last week, namely 0.05 to 0.08 parts per thousand, was so small that it might well be entirely accounted for by a very faint volatility of the substance when exposed to a low vacuum. But to make quite sure that if there were any water left occluded in the crystals it could only be in minute traces, the samples were dried for a further 6 hours in vacuo, at a temperature of 45°C. ± 5°C., and the heat of combustion determined directly afterwards in order to compare it with the value obtained by Verkade and Coops (8). The two groups of results are given in calories$_{15}$ in table 2, Verkade's values having previously been reduced to vacuo.

TABLE 1

Loss in weight of succinic acid (in powder) on standing over phosphoric anhydride in vacuo

INITIAL WEIGHT	LOSS	WEIGHT AFTER 11 DAYS	LOSS	WEIGHT AFTER 8 MORE DAYS	TOTAL LOSS	LOSS IN PARTS PER THOUSAND
grams	*mg.*	*grams*	*mg.*	*grams*	*mg.*	
3.9407	0.9	3.9398	0.2	3.9396	1.1	0.25 per cent
3.8036	0.7	3.8029	0.3	3.8026	1.0	

TABLE 2

Isothermal heat of combustion of succinic acid, per gram weighed in vacuo, at an initial temperature of 20°C.

THE AUTHOR'S VALUES	VALUES OF VERKADE AND COOPS
3025.2 3024.6 3024.9 (mean)	3026.1 3026.2 3026.1 3029.1 3026.9 (mean) 3026.1

It will be seen that the author's trial values are already very near to those of Verkade and Coops, more particularly to the first three which agree exceptionally well with one another while the fourth appears to be abnormally high. If, on the other hand, it is observed that the values of the Dutch investigators (obtained by the ordinary method) seem to be usually somewhat higher than those of the author (obtained by the adiabatic method), as illustrated before in the case of salicylic acid and naphthalene (3), it will appear that the sample of succinic acid derived in the way described from the starting material was either completely pure and dry or at least very nearly so.

Having thus satisfied himself about the apparent degree of purity of the B.D.H. preparation, by some very sensitive and independent test, the author proceeded with the preliminary examination of succinic acid from the point of view of its resistance to decomposition on heating in air or in vacuo. The stability on heating is indeed an important quality to be expected from a standard substance, as it affords a sure method to ascertain whether the drying has been carried to completion, without running the risk of deteriorating the substance. It is indeed only after such stability tests have proved satifactory that an apparently suitable substance becomes really interesting as a prospective standard and that its energy contents are shown to be worthy of a systematic study.

The stability tests now to be recorded are of two kinds: one series consists of the values obtained for the loss in weight experienced by two lots of pellets of the acid, of about 4 g. each (previously dried, when still in powder form, for four days at the ordinary temperature and then for 6 hours at a temperature in the neighborhood of 45°C.) on heating in vacuo over fresh phosphoric anhydride, to gradually increasing temperatures; the other series was obtained by determining the heat of combustion of various specimens of succinic acid after having subjected them under greatly reduced pressure to increasing temperatures. These data have been collected in tables 3 and 4.

It will be seen at once from the consideration of table 4 that the heat of combustion observed does not show any characteristic variation when the sample of succinic acid is gradually raised from the ordinary temperature to a temperature in the neighborhood of 130°C., the heating being combined with a reduction of pressure to about 0.1 mm. of mercury.

All of the results collected in tables 1, 2, and 4 prove conclusively that: (1) Succinic acid can be completely dried by heating for 6 hours in a vacuum at a temperature of 45 ±5°C. (2) The volatility of succinic acid is very small, even when it is heated in vacuo. (3) A statement recently published and according to which succinic acid, when heated in vacuo to a temperature of 55°C., would give an appreciable proportion of succinic anhydride is not justified. Indeed it can easily be calculated that the anhydrization of 1 gram of succinic acid to the extent of only 1 per cent would bring about an increase in the heat of combustion of 6.7 calories. No such change has obviously taken place during the heating; on the contrary, the mean values corresponding to the specimens which have been heated to temperatures ranging between 62°C. and 90°C. are, if anything, smaller than those corresponding to the temperature of 45°C. only.

Again, a portion of the acid (after recrystallization from conductivity water) was dried for 7 hours under atmospheric pressure at a temperature of about 130°C. (sample A) and another portion of the same sample to

TABLE 3

Loss in weight of succinic acid (in pellet form), on heating in vacuo (in presence of phosphoric anhydride) to the various temperatures recorded

INITIAL WEIGHT OF PELLETS	LOSS IN WEIGHT OF PELLETS			TOTAL LOSS IN WEIGHT	
	3 hours at 45 ± 5°C.	6 more hours at 45 ± 5°C.	6 hours at 62 ± 2°C.	In milligrams	Per 10.000
grams	*mg.*	*mg.*	*mg.*		
3.8853	0.2	0.5	0.4	1.1	2.5
3.5610	0.3	0.2	0.4	0.9	2.8

TABLE 4

Isothermal heat of combustion of succinic acid per gram weighed in vacuo, after heating in steps up to 130°C.

TEMPERATURE	HEATING INTERVAL	HEAT OF COMBUSTION	MEAN	SAMPLE
degrees C.	*hours*	*cal.₁₅*		
45 ± 5	6	3025.2 3024.6	3024.9	α
45 ± 5	12	3025.6 3026.3	3025.9	β
62 ± 3	6	3023.9 3024.2	3024.2	γ
68 ± 2	4	3023.9 3023.7	3023.8	δ
70 ± 2	6	3024.3 —	3024.3	δ′
90 ± 10	2	3021.5* 3023.5	3023.5*	ε
120 ± 10	4	3025.1 —	3025.1	φ

General mean for these preliminary combustions* = 3024.6 cal._{15}; mean error for mean = 0.09 part per thousand.

For the tenth of these combustions, it was observed that the bomb was slightly leaking at the end of the experiment, thus explaining the low value (3021.5); this result will consequently be neglected.

about 140°C. for a period of 6 hours (sample A_1), with the following results for the heats of combustion:

Sample	*Heat of combustion*	
A, dried at 130°C., no phosphoric anhydride	3024.8	3024.8 (mean)
	3024.7	
A_1, dried at 140°C., with phosphoric anhydride	3025.0	3025.2 (mean)
	3025.4	

However, on heating sample A for 3 hours at about 172°C., and subsequently to a still higher temperature, until the whole of the sample had melted, there was an unmistakable formation of succinic anhydride, as shown by the following values for the heat of combustion of these heated samples:

Sample	*Heat of combustion*		*Anhydride formation*
A′, heated at 172°C	3036.0	3035.6 (mean)	1.4 per cent
	3035.2		
A″, heated above melting point	3094		10 per cent (approximately)

III. CONFIRMATORY COMBUSTIONS WITH SAMPLES OF SUCCINIC ACID OBTAINED BY RECRYSTALLIZATION FROM SEVERAL SOLVENTS

The results from the combustions recorded up to the present have been obtained under somewhat varying conditions (namely with different amounts of substance and cotton burnt, i.e., for a different range of temperatures than the usual one, and also in connection with a small gradual variation in the value for the water equivalent); these differences will appear clearly from the comprehensive tables (7 and 8) summarizing the whole of the calorimetric data obtained with succinic acid.

At this juncture it appeared advisable to check under more standardized conditions the results collected so far (i.e., with succinic acid obtained by recrystallization from water), and also to find out whether the substitution for water of solvents with a lower boiling point,[3] but possessing at the same time a heat of combustion per gram much larger than that of succinic acid,[4] would affect them in any way.

1. Samples recrystallized from water

The starting material for the new combustions was sample A (dried under ordinary pressure at a temperature of approximately 130°C. for 7 hours). This sample was now heated in a vacuum for a period of 7 hours at a temperature of 52 ± 2°C (without phosphoric anhydride); sample B

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[3] Thus more easily got rid of and with less danger of decomposition for the substance.

[4] So that the presence of the merest trace of such solvents would quite easily reveal itself through a variation in the heat of combustion, this time however of opposite sign to that which might have been expected from the presence of traces of water.

obtained in that way was then heated in vacuo for 8 hours at a temperature of 80 ± 2°C. (in the presence of phosphoric anhydride), giving sample C; samples B and C were now burnt in duplicate directly after heating, and in the case of the latter the combustions were repeated after the pellets had stood for one month over phosphorus pentoxide (see sample C′). On the whole the results show a very good agreement amongst themselves: those obtained with samples dried in the presence of phosphoric anhydride (see samples A_1 and C) are higher by a few tenths of one calorie than those (relative to A and B) obtained in the absence of a drying agent; the difference, amounting to about 0.5 calorie in both cases, is however so small as to have only little significance. The final results obtained with succinic acid recrystallized from conductivity water have been collected in table 5.

TABLE 5

Isothermal heat of combustion of succinic acid, per gram weighed in vacuo, and dried for different lengths of time at the temperatures indicated

SAMPLE	DRYING TEMPERATURE	PRESSURE	DRYING AGENT	HEAT OF COMBUSTION
	degrees C.	*mm.*		*cal.$_{15}$*
A	ca. 130	760		3024.8 3024.7 } 3024.8 (mean)
A_1	ca. 140	760	P_2O_5	3025.0 3025.4 } 3025.2 (mean)
B	52 ± 2	0.15		3024.9 3025.5 } 3025.2 (mean)
C	80 ± 2	0.14	P_2O_5	3025.3 3026.3 } 3025.8 (mean)
C′	Standing one month		Old P_2O_5	3025.0 3025.9 } 3025.4 (mean)

General mean for the ten combustions = 3025.3 cal.$_{15}$ per gram in vacuo. Mean error for mean = 0.05 part per thousand.

2. *Recrystallization from solvents other than water*

The choice of a suitable solvent for succinic acid is very limited even if no additional conditions were required, as there are in the present case. Ether was selected in spite of its small solvent power for succinic acid on account of its large heat of combustion (8805), its very low boiling point, its inertness, and also its availability in a pure state. The small sample ω_1—derived from sample C and thus completely dry—was recrystallized, from ether (A.R.) and then entirely freed from traces of solvent by heating in a vacuum (0.15 mm.) for 4 hours at a temperature of 80 ± 2°C.

Another portion of the same sample C was recrystallized from purified acetone (boiling between 55.8 and 56.0°C.) which was selected as the second solvent for practically the same reasons as those given with reference to ether, with the useful difference that the solvent power of acetone is much more suitable than that of ether with respect to succinic acid. By heating the last lot of crystals for 5 hours in vacuo at a temperature of 77 ± 2°C., a sample ω_2 was obtained. The heat of combustion found for that sample (3026.5 and 3027.1; mean = 3026.8) was however larger by 1.5 calories than the mean just recorded for the ten final combustions with the samples prepared by recrystallization from water. This small discrepancy was probably due to the presence in the sample ω_2 of a faint trace of acetone. It can be calculated indeed that, owing to the relatively large heat of combustion of acetone (7351), it would suffice that 1 g. of succinic acid would contain only 1 mg. of acetone (i.e., one part per thousand) in order to increase the heat of combustion of the contaminated sample by 1.3 calories; this is just about equal to the divergence observed. As, however, the small discrepancy might have resulted from a slight measure of purification having taken place as the consequence of the substitution of acetone for water, it was considered worth while to repeat the crystallization from acetone with a fresh sample of succinic acid. The crystals from this new recrystallization were first dried for one night over filter paper in the air, then heated for 6 hours in vacuo to a temperature of 80 ± 2°C., with alternate crushing. The value now obtained for the heat of combustion of the new sample ω_2' (3025.6 and 3026.3; mean = 3025.8) being practically identical with the general mean (3025.3) obtained previously, it was clear that the slightly too large value found for the heat of combustion of the last sample but one (from the first recrystallization with acetone) was really caused by the presence of a minute trace of acetone in the sample. As a final confirmatory test for this statement a further recrystallization of the last sample was carried out, the crystals being heated in vacuo for 5 hours at a temperature of 83 ± 2°C.; the new sample (ω_2'') was now used for a last combustion, the result of which (3025.5) was entirely in agreement with the general mean determined previously.

The results obtained for the various combustions with samples derived from recrystallizations with ether or acetone have been collected in table 6.

It can be seen that this general mean, obtained from the five combustions carried out with samples of acid recrystallized from solvents other than water, is exactly the same as that (3025.3) obtained previously when the solvent was water. The mean of means (for the whole of the twenty-six combustions carried out successfully with fifteen different samples of succinic acid) is equal to 3025.0 calories$_{15}$: it differs only by +0.4, −0.3, and −0.4 calorie from the means referring respectively to the eleven preliminary and to the ten final combustions corresponding to solvent water, and to the five combustions corresponding to solvents ether or acetone. It can thus safely be concluded that the heat of combustion of succinic acid, per gram weighed in vacuo, and burnt isothermally at the initial temperature of 20°C. is genuinely equal to 3025 ± 1 calories$_{15}$.

IV. TECHNIQUE

1. *Apparatus*

An adiabatic calorimeter with a stirrer of the propeller type was used in conjunction with a Landrieu-Malsallez bomb (with gold lining and platinum electrodes); the jacket, of the submarine type, was heated electrolytically by means of a current of about 25 amperes (at 230 volts). The temperature rise was measured with a Beckmann thermometer having a range of about 5°C. (calibrated by the P.T.R. at each 0.1 division to the nearest thousandth of one degree).

TABLE 6

Isothermal heat of combustion of succinic acid per gram in vacuo, after recrystallization from ether (once) and acetone (twice)

SOLVENT	TEMPERATURE	TIME INTERVAL	HEAT OF COMBUSTION	
	degrees C.	*hours*	*cal.*$_{15}$	
Ether	80 ± 2	4	3024.9 3024.6	3024.7 (mean)
Acetone (once)	80 ± 2	6	3025.6 3026.3	3025.8 (mean)
Acetone (twice)	83 ± 2	5	3025.5	

General mean = 3025.4 cal.$_{15}$; mean error for mean = 0.1 per thousand.

2. *Method*

The "constant range method" first proposed by the author in 1926 (2) was usually adhered to. The normal range of 2°C. used in former work was again selected, starting from the same initial temperature of 19.7°C. In order to meet in advance the possible criticism that by using another range the results might be somewhat different, a larger range (2.6°C.) was used as well.

V. GENERAL INFORMATION; CALIBRATIONS; MAIN FEATURES OF THE COMBUSTIONS WITH SUCCINIC ACID

1. *General information*

In order to comply with the recommendations just adopted by the Commission Internationale Permanente de Thermochimie at a meeting held in Paris in April, 1933, the following data have been collected hereunder:

(a) The mass of substance burnt was approximately 1.35 g. of benzoic acid and 2.80 g. of succinic acid for the range of 2°C., against 1.75 g. of benzoic acid and 3.65 g. of succinic acid for the range of 2.6°C. (b) The weight of auxiliary substance (cotton thread or wool) varied between 3 and 6 mg. (c) The mass of water introduced into the bomb was 1 g. in every case. (d) The oxygen was introduced under a constant pressure of 35 atmospheres (±5 per cent). (e) The bomb had a capacity of 450 cc. (f) The initial temperature was 19.7°C. in every instance, while the final temperature was either 21.7°C. or 22.3°C., according to whether the range selected was 2°C. or 2.6°C.

The oxygen used in connection with all the combustions reported in this paper was manufactured (in the works of the British Oxygen Company Ltd.) by fractional distillation of liquid air. As will be shown elsewhere oxygen derived from that source contains traces of combustible impurities which are exceedingly difficult to detect (owing to the extreme precision required to bring this cause of error to light in a conclusive way), so much so that they do not make their influence felt to the same extent all through the life of the oxygen cylinder. This important and curious phenomenon has been studied very closely by the author during the last three years, using several different cylinders of oxygen. Its discussion and interpretation will form the subject of a separate paper to be published shortly.

2. Calibrations

In order to establish once and for all for the water equivalent a fixed value of reference relative to absolutely pure oxygen,[5] a special calibration had been carried out four years ago with a sample of the preparation No. 39c of benzoic acid supplied by the Bureau of Standards, using pure oxygen (purified by slowly passing the gas over palladiumized asbestos raised to a red heat); the true constant thus obtained for the water equivalent, after reduction to an isothermal value, was 4277.1 calories$_{15}$. The data relative to that calibration have been collected in table 7, combustions 1 to 5. Since however the combustions of succinic acid were to be carried out with a newly refilled cylinder of oxygen, it was necessary either to purify this oxygen (by preheating it under suitable conditions prior to filling the bomb) or to carry out a special calibration with it. Since the former operation is very tedious and troublesome, the latter alternative was preferred. Furthermore, since the range of 2.6°C. had not been investigated before and since, on the other hand, some doubt had been expressed recently from a continental laboratory as to the true identity of successive preparations of

[5] Thus allowing one, by comparison with the value found for the water equivalent obtained with some other oxygen, to estimate the approximate purity of the latter.

TABLE 7

Water equivalent (at the temperature of 20°C.) for pressure of 35 atmospheres in the bomb and for various pressures in the cylinder of oxygen (in cal.$_{15}$ and in vacuo)

NO.	WEIGHT	TEMPERATURE (CORRECTED FOR BORE)		CORRECTIONS IN TEN THOUSANDTHS			CORRECTED RISE IN °C.	CORRECTIONS IN CALORIES FOR		SAMPLE	PRESSURE	WATER EQUIVALENT (ISOTH.)	MEAN WATER EQUIVALENT
		Initial	Final	Range	Stem	Stirr.		HNO_3	Cotton				
1. (1929) Calibration with preheated oxygen for *range of 2°C.* (mean error for mean = 0.11 per thousand													
1	1.3406	2.0373	4.0205	139	−5	103	1.9845	8.15	10.2	39c	—	4277.4	4277.1
2	1.3444	1.9517	3.9447	140	1	123	1.9921	—	19.4	—	—	4278.0	
3	1.3432	1.9214	3.9178	—	—	168	1.9901	8.4	15.0	—	—	4276.3	
4	1.3458	1.9135	3.9095	—	—	122	1.9953	8.6	19.0	—	—	4275.6	
5	1.3452	1.9244	3.9267	—	−1	200	1.9918	7.7	13.8	—	—	4278.0	
2. (1933) Calibration *with new and non-preheated* oxygen for *range of 2.6°C.* A. For pressure in cylinder = 116 to 113 atmospheres and 112 to 109 atmospheres. General mean (for combustions 6 to 13) = 4277.1 with mean error for mean = 0.06 per thousand													
6	1.7550	1.9031	4.4861	181	0	49	2.5962	1.8	12.6	48a	116	4276.3	4277.0 4277.1
7	1.7546	1.9059	4.4908	—	—	77	2.5953	1.1	—	—	115	4276.5	
8	1.7543	1.9962	4.5810	—	—	86	2.5943	2.2	—	—	114	4277.8	
9	1.7531	1.9078	4.4935	—	—	97	2.5941	1.6	—	—	113	4277.4	
10	1.7533	1.9070	4.4909	181	0	86	2.5934	2.0	12.6	39b	112	4276.8	4277.2
11	1.7533	1.9021	4.4843	—	—	71	2.5932	1.9	—	—	111	4277.0	
12	1.7524	1.9058	4.4847	—	—	48	2.5922	1.6	—	—	110	4276.5	
13	1.7539	1.9017	4.4826	—	—	58	2.5932	1.7	—	—	109	4278.7	
B. For pressure in cylinder = 93 to 87 atmospheres. Mean error for mean = 0.09 per thousand													
14	1.7521	1.9036	4.4821	181	0	45	2.5921	1.5	15.0	39b	93	4276.7	4276.6
15	1.7530	1.8941	4.4738	—	—	38	2.5940	1.1	—	—	92	4275.6	
16	1.7487	1.9092	4.4821	180	1	48	2.5862	0.9	12.6	—	88	4277.0	
17	1.7533	1.8965	4.4766	181	0	51	2.5931	1.8	13.0	—	87	4277.3	
3. (1933) Calibration with same oxygen as in § 2, but for *range of 2.0°C.* A. For pressure in cylinder = 66 to 64 atmospheres. Mean error for mean = 0.08 per thousand													
18	1.3428	1.8973	3.8743	138	0	42	1.9866	1.4	7.8	39b	66	4275.1	4275.1 4275.2
19	1.3413	1.8976	3.8723	—	—	44	1.9841	1.6	8.2	—	65	4275.4	
20	1.3456	1.8979	3.8798	139	—	48	1.9910	1.5	7.0	—	—	4274.2	
21	1.3466	1.8996	3.8826	—	−1	53	1.9915	1.7	6.6	—	64	4275.7	
B. For pressure in cylinder = 54 to 39 atmospheres. Mean error for mean = 0.02 per thousand													
22	1.3433	1.9028	3.8832	139	0	68	1.9875	0.7	9.2	39b	54	4275.1	4275.3
23	1.3458	1.8928	3.8763	—	—	63	1.9911	—	9.4	—	45	4275.4	
24	1.3433	1.8991	3.8784	—	−1	56	1.9875	—	—	—	39	4275.3	

General mean (for combustions 18 to 24) = 4275.2 cal.$_{15}$ with mean error for mean = 0.04 per thousand standard benzoic acid issued by the Bureau of Standards, it was considered desirable to carry out two independent calibrations for the same range of 2.6°C., one with the preparation 39b and the other with the preparation 48a. The combustions made with the latter (see table 7, Nos. 6 to 9) gave for the water equivalent the value 4277.0, while with the former the value 4277.2 was obtained (see Nos. 10 to 13 of the same table). The mean for these eight combustions is 4277.1; it is thus identical with the value found four years earlier wth the same calorimetric system but for a range of 2°C. and with purified oxygen. This striking agreement establishes a very strong probability in favor of the purity of the oxygen used for the present research and at the same time proves that the preparations 39b, 39c, and 48a of standard benzoic acid supplied at various times by the Bureau of Standards are really identical, at least in so far as their energy contents are concerned.

But for the reason already stated that the value for the water equivalent changes appreciably as a rule when the pressure in the oxygen cylinder decreases, five more series of control calibrations were carried out for different pressures in the cylinder. Three out of these were especially carried out in connection and simultaneously with the actual combustions of succinic acid; they have for that reason been introduced in this paper (see table 7, Nos. 14 to 24). It will appear from a consideration of the last column of table 7 that in the particular case of the oxygen used for this investigation there has been a gradual decrease of some 2 calories as the pressure in the cylinder dropped from 116 to 35 atmospheres.

3. Combustions of succinic acid

Simultaneously with these calibrations, three series of combustions were carried out with succinic acid under conditions as identical as possible, in particular with respect to the two selected ranges of 2.0°C. and 2.6°C. The data relative to these experiments have been collected in table 8.

VI. GENERAL CORRECTIONS

1. Reduction to vacuo of the weights of substance burnt

(a) The density of benzoic acid was taken as equal to 1.266 (cf. International Critical Tables, Vol. I, p. 77), so that the corrective terms to be added to the weights in air (1.75 and 1.35 g.) of benzoic acid required for the two ranges of 2°C. and 2.6°C., are 1.4 and 1.1 mg., respectively.

(b) The density of succinic acid was taken as equal to 1.56 (same reference), so that the corrective terms for 3.65 and 2.80 g. of this acid are 2.3 and 1.77 mg., respectively.

(c) The weights of cotton were so small that the vacuum reduction term was quite insignificant.

TABLE 8

Isothermal heat of combustion (at constant volume) per gram of succinic acid (weighed in vacuo) at a temperature of 20°C., expressed in cal.$_{15}$

NO.	WEIGHT	TEMPERATURE (CORRECTED FOR BORE)		CORRECTIONS IN TEN THOUSANDTHS			CORRECTED RISE IN °C.	CORRECTIONS IN CALORIES FOR		SAMPLE	PRESSURE	ISOTHERMAL HEAT OF COMBUSTION	MEAN HEAT OF COMBUSTION	WATER EQUIVALENT USED
		Initial	Final	Range	Stem.	Stirr.		HNO_3	Cotton					
25	3.6545	1.9067	4.4826	180	1	51	2.5889	0.7	20.6	α	98	3025.2	3024.9	4276.6
26	3.6570	1.9061	4.4858	—	0	45	2.5932	14.9	19.4	—	97	3024.6		—
27	3.6595	1.9008	4.4802	—	—	42	2.5932	1.0	22.0	β	95	3025.6	3025.9	—
28	3.6591	1.9049	4.4849	—	—	45	2.5935	0.9	—	—	94	3026.3		—
29	3.6596	1.9084	4.4867	—	—	48	2.5915	0.8	20.8	γ	82	3023.9	3024.1	—
30	3.6590	1.9088	4.4861	—	—	43	2.5910	0.6	19.4	—	81	3024.2		—
31	3.6621	1.9066	4.4896	181	1	93	2.5919	1.6	14.2	δ	80	3023.9	3023.8	—
32	3.5987	1.9061	4.4398	177	0	45	2.5469	0.8	—	—	80	3023.7		—
33	3.6581	1.8970	4.4721	180	1	39	2.5893	1.2	—	δ'	78	3024.3	3024.3	—
34	3.6584	1.8918	4.4769	—	0	45	2.5886	0.7	13.4	ϵ	73	3023.5	3023.5	—
35	3.6492	1.8965	4.4657	—	—	38	2.5834	0.9	13.0	φ	72	3025.1	3025.1	—

General mean (for the eleven preliminary combustions nos. 25 to 35, range = 2.6°C.) = 3024.6 cal.$_{15}$

NO.	WEIGHT	Initial	Final	Range	Stem.	Stirr.	CORRECTED RISE IN °C.	HNO_3	Cotton	SAMPLE	PRESSURE	ISOTHERMAL HEAT OF COMBUSTION	MEAN HEAT OF COMBUSTION	WATER EQUIVALENT USED
36	2.8058	1.9010	3.8819	138	0	66	1.9881	0.6	14.6	A	61	3024.8	3024.8	4275.2
37	2.8062	1.8998	3.8820	—	—	76	1.9884	0.4	15.0	—	60	3024.7		—
38	3.6589	1.8987	4.4756	180	—	43	2.5906	1.2	14.2	A_1	69	3025.0	3025.2	—
39	3.6565	1.8973	4.4730	—	—	45	2.5892	0.8	—	—	—	3025.4		—
40	2.8051	1.9488	3.9284	138	1	61	1.9874	0.7	13.4	B	63	3024.9	3025.2	—
41	2.8046	1.9017	3.8819	—	0	63	1.9877	0.5	14.6	—	62	3025.5		—
42	2.8070	1.9049	3.8871	—	—	68	1.9892	0.6	14.2	C	57	3025.3	3025.8	—
43	2.8036	1.9001	3.8808	—	—	70	1.9875	0.9	—	—	56	3026.3		—
44	2.8067	1.8996	3.8808	—	—	60	1.9890	0.7	15.4	C′	42	3025.0	3025.4	—
45	2.8067	1.9020	3.8827	—	—	49	1.9896	0.6	—	—	—	3025.9		—

General mean (for the ten final combustions nos. 36 to 45, usual range = 2.0°C., solvent water) = 3025.3 cal.$_{15}$. Mean error for mean = 0.05 part per thousand

NO.	WEIGHT	Initial	Final	Range	Stem.	Stirr.	CORRECTED RISE IN °C.	HNO_3	Cotton	SAMPLE	PRESSURE	ISOTHERMAL HEAT OF COMBUSTION	MEAN HEAT OF COMBUSTION	WATER EQUIVALENT USED
46	2.8068	1.8988	3.8786	138	1	48	1.9889	0.7	15.0	ω_1	47	3024.9	3024.7	4275.2
47	2.8080	1.8986	3.8789	—	0	45	1.9896	0.6	—	—	—	3024.6		—
48	2.8063	1.8994	3.8818	—	—	72	1.9890	0.8	14.6	ω'_2	41	3025.6	3025.8	—
49	2.8054	1.9022	3.8868	—	—	94	1.9890	1.0	15.0	—	40	3026.3		—
50	2.8041	1.8987	3.8791	—	−1	65	1.9876	0.9	15.4	ω''_2	39	3025.5	3025.5	—

General mean (for the five final combustions nos. 46 to 50, range = 2.0°C., solvent ether or acetone) = 3025.4 cal.$_{15}$. Mean error for mean = 0.1 part per thousand. Mean of means (for the whole twenty-six combustions) = 3025.0 cal.$_{15}$ with mean error for mean of mean of 0.05 per thousand.

2. Reduction of the heat of combustion of succinic acid to its isothermal value

In a paper which will appear shortly elsewhere, the author has shown that, for a substance of gram-molecular weight M and heat of combustion (per gram) Q, and whose empirical formula is $C_aH_bO_cN_d$, the corrective term to be added to the value observed for the water equivalent (when determined as per international agreement by means of standard benzoic acid, whose heat of combustion is taken as 6319 calories$_{15}$ per gram) in order to give it the value which corresponds to an isothermal combustion for succinic acid is given by

$$\mathrm{corr.}_{\mathrm{is.}} = \left(- \frac{1.7a + 7.75b + 2.5(c + d)}{M} \cdot \frac{1}{Q} - \frac{0.52}{631} \right) W \cdot \Delta t$$

where Δt represents the rise in °C. and W stands for the water equivalent in calories per degree. Hence, for succinic acid ($M = 118$; $Q = 3025$ calories per degree) whose formula is $C_4H_6O_4$, the corrective term (to be added to the water equivalent) is either $1.98 - 0.92 = 1.06$ calories per degree (for $\Delta t = 2.6$°C.) or $1.5 - 0.7 = 0.8$ calorie per degree (for $\Delta t = 2$°C.).

3. Correction for the temperature coefficient of the heat of combustion

The correction is nil in this case, since the value (6319) used for the heat combustion of benzoic acid refers to an isothermal combustion at the temperature of 20°C. and both series of combustions with either succinic acid or benzoic acid were carried out at practically the same initial temperature (19.7°C.).

4. Correction for the formation of nitric acid

For work of the highest precision it is necessary to reduce to as low a value as possible the correction for the formation of nitric acid, owing to the fact that this correction is always somewhat ill-defined. This result can be achieved by making use exclusively of nitrogen-free oxygen (or at least oxygen containing only very minute traces of nitrogen) and by sweeping the air out of the bomb prior to its filling. When, as is the case here, the volatility of the substance under investigation is very small, the same result may be obtained more easily by evacuating the bomb for a very short while under well standardized conditions.

For the actual calculation of the correction allowing for the formation of traces of nitric acid, the heat of formation of the latter under the conditions of dilution normally prevailing in the bomb was taken as equal to 230 calories per gram of acid (formed from $N + O + H_2O$).

5. Correction for the heat evolved by the combustion of the auxiliary substance used for ignition

For the present research, both cotton wool and cotton thread were used. Two auxiliary combustions were made in order to determine the heat of combustion of the two forms of cotton used for ignition: for the wool, the heat of combustion was found to be 3954 calories per gram, while the value 3990 calories was obtained for the thread.

6. *Corrections for incomplete combustion*

Tests for complete combustion were carried out in a certain number of cases taken at random. The residual gases when bubbled at a very low speed through palladium chloride solution failed to indicate the presence of the merest traces of carbon monoxide.

7. *Correction for the Joule effect in the ignition wire*

The platinum wire used for the present work was exceedingly fine (viz., 0.03 mm. in diameter); the time required to fuse the length of wire (about 1 cm.) stretching between the two platinum electrodes was so small as to make the corrective term for the Joule effect entirely negligible.

VII. COMPARISON BETWEEN THE RESULTS OBTAINED FOR THE HEAT OF COMBUSTION OF SUCCINIC ACID BY THE AUTHOR AND OTHER OBSERVERS

Stohmann, Kleber, and Langbein (6) found for the heat of combustion of succinic acid the value 3022 calories$_{15}$, with a maximum deviation of 1.1 per thousand. This result is only smaller by about 3 calories than that of the author, the difference being remarkably small considering that the work of the German pioneers was done nearly half a century ago!

Louguinine (5) found two values, differing by 12 calories from one another, the highest of the two being still lower than that of the author by 10 calories. These results of Louguinine, like much of his work are characterized by a large maximum deviation (4.2 per thousand in his latest series of combustions with succinic acid) and have no more than a historical value!

Verkade, Hartmann, and Coops (9), on the contrary, made some trustworthy determinations—unfortunately only four in number—with two different samples of succinic acid; the general mean for their four combustions was 3026.9 calories$_{15}$, with a mean error of the mean of 0.25 per thousand and a maximum deviation from the mean of 0.75 per thousand. As already observed on page 4, the value of Verkade is higher than that found by the author by only 1.5 calories, in spite of the fact already mentioned that his fourth value (3029.1) is abnormally large and stands in sharp contrast with the three others, which are identical (3026.1). It can therefore be safely concluded that Verkade's value (3026 to 3027) is as near to that of the author (3025 ± 1) as can reasonably be expected, especially when it be remembered that the Dutch investigators used a different method (the non-adiabatic!) and worked otherwise under slightly different conditions.

More recently still, Beckers (10) found for various specimens of succinic acid values which vary between 3024.4 and 3027.4 calories$_{15}$. The final value given in the present paper (3025.0 ± 1) is thus lying well within that interval.

VIII. SUCCINIC ACID POSSESSES THE MULTIPLE QUALITIES WHICH RENDER IT SUITABLE AS A CALORIMETRIC STANDARD

The conditions which succinic acid will have to fulfill in order to be acceptable as a calorimetric standard will now be considered in turn.

1. It should be easily obtainable in an exceptionally pure state

Succinic acid will have no difficulty to establish its claim in that respect as will appear from a rapid consideration of the specifications given by the British Drug Houses for their A.R. preparation. The maximum limits of impurities allowed are: 0.05 per cent of ash (on 1 g.); 0.003 and 0.005 per cent of chlorides and sulfates, respectively (on 1 g. of acid in 20 cc. of water). Actually, the tests carried out by the author for ash, first on 1 g. and afterwards on 5 g., were entirely negative, as well as the tests for chlorides and sulfates.

It may also be recalled here that the successive recrystallizations of the original preparation, first from water and then from ether and acetone (the latter solvent being used twice), failed to show any significant variation in the value for the heat of combustion, thus giving much support to the claim of absolute purity of the substance.

2. It should be easy to dry and should remain so without requiring special precautions for keeping

It has been mentioned already that succinic acid, even when recrystallized from water, could easily be obtained in a perfectly dry condition, either by heating to a temperature of 130 to 140°C. in air or to a temperature of about 50°C. in vacuo.

The proof that succinic acid is not at all hygroscopic is given by the following results, obtained by allowing two pellets of about 1 g. to stand over night in a moist atmosphere such as that provided by a desiccator containing a dish full of water. The gain in weight was only 0.01 and 0.00 per cent for the two pellets respectively, thus giving an average gain of 0.005 per cent in 24 hours; this is just within the experimental error relative to weighings.

3. It should be perfectly stable in air, even at temperatures above 100°C., so as to allow of thorough drying

The proof that this condition is completely fulfilled by succinic acid lies in the fact that the heat of combustion of succinic acid does not change measurably when it is heated to 140°C. (for 6 hours) under atmospheric pressure or to about 120°C. (for 4 hours) under a pressure reduced to approximately 0.1 mm. of mercury.

4. It should not be volatile

It has been found that samples of about 4 g. of succinic acid, either in the form of finely crushed powder or in pellets, lost only one part in 10.000 after being left for a fortnight in an evacuated desiccator over phosphoric anhydride.

The volatility of succinic acid, at ordinary temperature and even in vacuo, is thus exceptionally small.

5. It should be easily compressible into firm pellets

Whether the pellets of succinic acid were made after a preliminary grinding to an exceedingly fine powder or whether they were prepared directly from the larger crystals, there never arose any difficulty during the removal of the pellets from the pellet press or during subsequent manipulations. Dozens of them were seized with the forceps to and from the balance pans without any loss of material being ever measurable; some were placed in the crucible inside the bomb and oxygen admitted swiftly into the latter, without any loss of weight being experienced. In short the pellets of succinic acid behaved in all respects quite as satisfactorily as those made with benzoic acid.

6. It should be easily inflammable

The fact that some difficulty was experienced at the beginning of the first series of combustions when cotton wool was used for ignition purposes cannot be considered, in the authors' opinion, as an argument in favor of the contention that succinic acid may be somewhat deficient from the point of view of its inflammability, as has been stated about some other substances (sucrose in particular!) which possess only a small heat of combustion per gram. Indeed, succinic acid can be ignited with great ease when a suitable igniter is used, and it is not necessary to employ an unduly large quantity of igniter, since less than 4 mg. of thread was found to be always quite sufficient.

7. It must be of such a nature as will favor complete combustion

As already mentioned, all tests for carbon monoxide gave negative results; nor were deposits of unburnt carbon ever left behind.

As a corollary to the last condition, the substance should obviously not possess the tendency to project small particles of its own substance out of the crucible, before burning. The excellent agreement obtained between individual results for the heat of combustion of the acid from some thirty combustions proves quite peremptorily that such an eventuality is not likely to arise with succinic acid.

IX. CONCLUSION

Succinic acid has been shown to fulfill to a high degree all the conditions which may reasonably be required from a calorimetric standard: in particular, it has given for the heat of combustion of fifteen different samples values which show a remarkable agreement amongst themselves. Even when the values of different observers are considered, there is undoubtedly a definitely better agreement between the modern ones as there is in the case of the other prospective auxiliary standard, namely, salicylic acid: the first is markedly more stable on heating than the latter and consequently much easier to dry thoroughly and without fear of decomposition; further, the purity of succinic acid may always be tested by way of an accurate titration, which is not the case with salicylic acid.

In conclusion, the author proposes to adopt formally succinic acid as a secondary calorimetric standard for bomb calorimetry and to accept for its isothermal heat of combustion at the temperature 20°C. the value 3025 ± 1 calories$_{15}$ (per gram weighed in vacuo).

The author desires to express his sincere thanks to Professor E. C. C. Baly, F. R. S., Head of the Inorganic Department, for laboratory facilities generously provided for the present investigation.

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HIGH TEMPERATURE CATALYSTS FOR CARBON MONOXIDE OXIDATION

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Received July 14, 1933

The investigations of Lamb, Bray, and Frazer (20) on catalysts for the oxidation of carbon monoxide resulted in a mixed oxide catalyst, Hopcalite, which completely oxidized carbon monoxide in air at room temperature and below. Since then numerous materials have been tested by different investigators, and in most instances oxide catalysts have proved superior. Bray and Doss (7) and Almquist and Bray (2) studied copper oxide and manganese dioxide. Bone and Andrew (6) studied nickel and copper and their oxides as catalysts. Taylor and Jones (29) also investigated copper and copper oxide catalysts, while Benton (5) made a study of several oxides and mixtures. Frazer (12), Whitesell and Frazer (31), Bennett (3), and Loane (23) have shown that highly purified oxide catalysts are more active than mixtures and that the activity depends more on the purity than on promoter action.

However, all the catalysts discussed above lose their activity on heating to elevated temperatures, owing either to sintering or to a change in chemical composition. Recently some attention has been directed toward catalysts which would stand heat treatment. Engelder and Miller (10) reported tests of a number of mixed oxides, the best being a mixture of copper and titanium oxides. Engelder and Blumer (9) found that a catalyst composed of cobaltic and ferric oxides was 100 per cent efficient at room temperature and could stand heating to 890°C. without a decrease in activity. Frazer (11) and Lory (24) have investigated the metal chromites and found them to be moderately active after heating to high temperatures.

In the present investigation catalysts of the oxide type and catalysts of the chromite type were studied, and it will be convenient to discuss them under two classifications according to whether they were supported or unsupported.

The catalysts were tested by the method described by Loane (23).

UNSUPPORTED CATALYSTS

Chromites

The chromites were prepared by the ammonium chromate method which has been used in different modifications by Lazier (22), Adkins and his coworkers (1, 8), and Lory (24). Molar weights of chromic anhydride and the metal nitrate were dissolved in water, precipitated with 3 moles of ammonium hydroxide, the precipitate filtered, washed with 250 cc. of water, and dried in an oven at 100°C. The metal ammonium chromate was decomposed by heating small portions carefully in a covered dish. The resulting chromite was heated for an hour in a crucible furnace.

Nickel chromite No. 1, copper chromite No. 1, cobalt chromite No. 1, and zinc chromite No. 1 were leached with hydrochloric acid until the excess metal oxide was dissolved out.

Cobaltites

Holgersson and his coworkers (17) report the formation of cobaltites, MCo_2O_4, when a divalent metal nitrate and cobalt nitrate in a 1:2 mole ratio are dissolved in water, evaporated, the nitrates decomposed, and the resulting mixture of oxides heated to 800–850°C. for a few hours. Natta and his coworkers (26, 27) have examined the structure of these compounds by means of the x-ray. They found them to be spinel-type compounds with a general formula $M^{++}O \cdot M_2^{+++}O_3$.

Iron cobaltite No. 2 and zinc cobaltite No. 2 were prepared by Holgersson's method. The others were prepared by dissolving the nitrates in a 2:1 mole ratio of cobalt and the other metal in water, adding a sufficient excess of ammonia to dissolve nearly all the original precipitate and form the ammonia complex (in the case of iron, naturally only the cobalt dissolved and formed the ammonia complex), evaporating the solution to dryness, decomposing the residue, and finally heating in the crucible furnace. This method gave a more finely divided, and to some extent more active, catalyst than the evaporation of the nitrates.

Ferrites

S. Hilpert (15) and Suzanne Veil (30) report the formation of ferrites by heating the mixed oxides to 900°C. Natta and Passerini (25) and Holgersson (16) have studied the crystal structure by means of x-rays and have found spinel forms.

Cobalt ferrite No. 1, copper ferrite No. 1, nickel ferrite No. 1, and manganese ferrite No. 1 were prepared by dissolving the nitrates of iron and the other metal in a 2:1 mole ratio in water, evaporating to dryness, decomposing the nitrates by heating, and finally heating the mixed oxides to the desired temperature. The ferrites No. 2 were prepared by precipitating the hydroxides from a solution of the nitrates or chlorides in a 2:1 mole ratio. The resulting hydroxides were filtered, washed with hot water, dried, and heated in the crucible furnace. Cobalt ferrite No. 2-B was washed with hot water after the final heating until the filtrate showed no test for chlorides, then heated again to 975°C.

Manganites

Cobalt manganite No. 2 was prepared according to Gmelin (13). Twenty-one grams of cobalt sulfate and 12 g. of potassium permanganate were dissolved in 600 cc. of water. Six hundred cc. of 3 per cent hydrogen peroxide were then added. The precipitate was filtered, washed free of sulfates, dried, and heated. The copper–cobalt manganite was prepared according to the directions in the patent of the I. G. Farbenindustrie (18). To 500 cc. of a saturated solution of potassium permanganate was added 60 g. of cobalt sulfate and 50 g. of copper sulfate. Hydrogen peroxide was then added until the permanganate color was discharged. The precipitate was filtered, washed free of sulfates, dried, and heated. The copper manganite and cobalt manganite No. 1 were made similarly.

Aluminates

The aluminates may be prepared by heating the mixed oxides in the correct mole ratios. Hedvall (14) has prepared many of these and Holgersson (16) and Natta and Passerini (25) report spinel structures from x-ray studies. Most of the aluminates have very distinctive colors.

Copper aluminate No. 2 and nickel aluminate No. 2 were prepared from a solution of the nitrates in a 2:1 mole ratio of aluminum and the other metal by adding ammonium hydroxide to a slight excess and precipitating the hydroxides. The mixed hydroxides were filtered off, washed, dried, and heated. The other aluminates were prepared by evaporating the solution of the nitrates to dryness, decomposing the nitrates, and heating.

The results of the tests of the efficiency of the unsupported catalysts are summarized in table 1.

SUPPORTED CATALYSTS

Aluminum oxide was used as the support. A ready supply was found in Hydralo, a commercial granular and porous product containing some silica. Precipitated alumina was also used. Inasmuch as Hydralo takes up moisture from the air very readily, it was necessary to heat the catalysts and let them cool in a dry atmosphere just before testing. Moisture acted as a poison for these catalysts at moderate temperatures.

The supported cobalt catalysts were the same color as cobalt aluminate and apparently consisted of a surface layer of cobalt aluminate on the alumina.

Cobalt aluminate No. 3

To 10 g. of Hydralo was added 6 g. of cobalt nitrate dissolved in 40 cc. of water. The mixture was evaporated to dryness, the nitrates decomposed, and the material heated to 1000°C. for 1 hour.

TABLE 1

Efficiency of unsupported catalysts

CATALYST	HEATED 1 HOUR AT °C.	PER CENT OF CARBON MONOXIDE CONVERTED AT						
		50°C.	100°C.	150°C.	200°C.	250°C.	300°C.	350°C.
Cobalt chromite No. 1	1000	0	0	0	55	100	—	—
Copper chromite No. 1	1000	0	8	60	100	—	—	—
Nickel chromite No. 1	1000	0	0	0	15	62	100	—
Nickel chromite No. 2	700	0	0	11	45	94	100	—
Zinc chromite No. 1	725	0	0	8	22	73	100	—
Zinc chromite No. 2	725	0	8	25	41	48	65	100
Mixed copper-cobalt chromite No. 1	325	40	100	—	—	—	—	—
Mixed copper-cobalt chromite No. 2	750	15	70	100	—	—	—	—
Copper cobaltite No. 1	950	0	10	78	100	—	—	—
Nickel cobaltite No. 1	950	0	30	80	100	—	—	—
Iron cobaltite No. 1	925	0	8	50	100	—	—	—
Iron cobaltite No. 2	925	0	15	55	100	—	—	—
Zinc cobaltite No. 1	925	0	20	62	100	—	—	—
Zinc cobaltite No. 2	925	0	10	60	100	—	—	—
Cobalt ferrite No. 1	975	0	0	18	66	100	—	—
Cobalt ferrite No. 2-A	700	0	2	16	50	90	100	—
Cobalt ferrite No. 2-B	975	0	0	21	60	90	100	—
Copper ferrite No. 1	975	0	0	7	41	87	100	—
Copper ferrite No. 2	700	0	4	25	68	87	100	—
Nickel ferrite No. 1	975	0	0	4	17	46	82	100
Manganese ferrite No. 1	975	0	0	0	6	15	38	58
Copper cobalt manganite No. 1	1000	0	0	3	12	23	42	59
Copper manganite No. 1	1000	0	0	78	100	—	—	—
Cobalt manganite No. 1	1000	0	0	18	45	77	94	100
Cobalt manganite No. 2	1000	0	0	2	7	30	57	78
Cobalt aluminate No. 1	975	45	70	100	—	—	—	—
Copper aluminate No. 1	975	0	0	25	100	—	—	—
Copper aluminate No. 2	975	0	8	75	100	—	—	—
Manganese aluminate No. 1	975	0	0	18	62	100	—	—
Nickel aluminate No. 1	975	0	0	9	58	90	100	—
Nickel aluminate No. 2	975	0	0	18	54	100	—	—
Zinc aluminate No. 1	975	0	0	0	0	0	0	28
Iron aluminate No. 1	975	0	0	6	25	70	100	—

Cobalt aluminate No. 4

A fresh layer of alumina was put on the surface of the Hydralo by adding 3 g. of aluminum nitrate in water to 10 g. of Hydralo, evaporating to dryness, and heating to 1000°C. This Hydralo was then treated as above.

Cobalt aluminate No. 5

Sixty-five grams of aluminum sulfate and 1.5 g. of cobalt nitrate were dissolved in 1000 cc. of water and ammonia added until just alkaline. The precipitate was washed, dried, heated to 1000°C. for 1 hour, washed until free from sulfate, heated to 1000°C. again, allowed to stand overnight in an ammoniacal solution of cobalt nitrate, washed until free from ammonia, and finally heated at 1000°C. for 1 hour.

Kleinstuck (19) reported that alumina took up metals from ammoniacal solutions of their salts and on ignition gave characteristic colors. He also mentioned that the blue-green copper compound oxidized warm methyl alcohol. Schenk (28) found that if not more than 5 per cent copper oxide was present in a precipitated mixture of copper and aluminum oxides the resultant mixture was grayish blue on ignition. The copper catalysts prepared were all bluish green in color. If too much copper were put in, they turned brown like copper aluminate. The catalyst was apparently a finely divided stabilized copper oxide.

Copper oxide No. 1

Ten grams of Hydralo was put in a solution of 2 g. of copper nitrate in 20 cc. of water. The mixture was evaporated, the nitrates decomposed, and heated to 925°C. for 1 hour.

Copper oxide No. 2

Two grams of aluminum nitrate in 20 cc. of water was added to 10 g. of Hydralo. The solution was evaporated to dryness, nitrates decomposed, and heated to 1000°C. for 1 hour. It was then put into a solution of 2 g. of copper nitrate in 20 cc. of water, evaporated to dryness, nitrates decomposed, and heated to 1000°C. for 1 hour.

Copper oxide No. 3

Ten grams of Hydralo was treated with a small amount of sodium silicate solution and heated to 1000°C. It was then put in a copper nitrate solution and the solution evaporated to dryness carefully so as not to decompose the nitrates. The residue was washed with water until the wash water showed no copper. The residue was dried and heated to 1000°C. for 1 hour.

Copper oxide No. 4

Ten grams of Hydralo was treated with ammonium hydroxide solution, the ammonia poured off, and immediately aluminum nitrate solution was added. This formed a gelatinous alumina around the Hydralo. This was washed, allowed to stand in copper nitrate solution, then washed until the wash water was free from copper, dried, and heated to 1000°C.

Copper oxide No. 5

Ten grams of Hydralo was allowed to stand in aluminum nitrate solution for several minutes and was then transferred into ammonium hydroxide solution. It was treated with an ammoniacal solution of copper nitrate, washed until free from alkali, dried, and heated to 1000°C.

Copper oxide No. 6

About 75 g. of anhydrous aluminum chloride was dissolved in 1500 cc. of water. The solution was heated to boiling and ammonia was added until the solution was decidedly alkaline. Then an ammoniacal solution of copper chloride was added until the supernatant liquid was dark blue. The precipitate was washed by decantation until free from alkali, filtered, washed, dried, and heated to 1000°C. for 1 hour.

TABLE 2

Efficiency of supported catalysts

CATALYST	TEMPERATURE OF TEST	PER CENT CONVERSION
	degrees C.	
Cobalt aluminate No. 3	157	75
Cobalt aluminate No. 4	164	100
Cobalt aluminate No. 5	90	100
Copper oxide No. 1	161	50
Copper oxide No. 2	124	75
	154	100
Copper oxide No. 3	100	90
	118	100
Copper oxide No. 4	26	50
	70	100
Copper oxide No. 5	25	50
	55	75
Copper oxide No. 6	26	50
	70	100

OXIDATION WITH NITROUS OXIDE

In order to arrive at some mechanism for the catalytic action of the various catalysts, it was decided to use some other source of oxygen than that of the air. So a 40:60 mixture of nitrous oxide and nitrogen was used with 1 per cent carbon monoxide. The temperatures of 100 per cent oxidation in nitrous oxide and in air are given in table 3.

It will be noticed that the chromites, cobaltites, and manganites give 100 per cent oxidation at temperatures rather close together, while with the aluminate and the copper oxide there is a wide discrepancy. In the first class are those compounds whose metal anion has a variable valence while in the other no such possibility exists. Lory (24) has shown that with air the chromites form a surface chromate which may be leached off with hot water. The amount of chromate may be determined by adding potassium iodide and titrating the liberated iodine with thiosulfate. Chromate formation was likewise proved here with the nitrous oxide. Five grams of copper chromite No. 1 was heated to 300°C. for 2 hours, leached with hot water, and chromate equivalent to 11.5 cc. of 0.01 *N* thiosulfate was obtained. It was heated again to 300°C. and then put in the nitrous oxide-nitrogen-carbon monoxide gas stream at 193°C. for 3 hours. At the end of that time a test showed 100 per cent oxidation of the carbon monoxide. The chromite was leached and showed a chromate equivalent of 5.8 cc. of thiosulfate. It was dried at 90°C. and then leached, showing a chromate equivalent of 0.8 cc. of thiosulfate. It was dried again at 90°C. and put in the train as before. After 4 hours in the gas stream at 196°C. the catalyst showed 100 per cent conversion. It was removed and leached and showed 2.2 cc. thiosulfate or nearly three times the amount of the blank (0.8 cc.). This indicates that the nitrous oxide oxidizes the chromite analogously to air, but not quite all the surface is oxidized,—only the more active spots and apparently these are the catalytically active spots. While the carbon monoxide is capable of reducing the whole surface, only the more active parts are oxidized by nitrous oxide and serve for catalysis. This serves to bear out further Lory's theory of alternate oxidation and reduction of the catalyst surface.

TABLE 3

*Comparison of oxidation with nitrous oxide and air**

CATALYST	TEMPERATURE AT 100 PER CENT OXIDATION	
	Air	N_2O
Copper chromite No. 1	181	182
Cobalt chromite No. 1	252	250
Copper cobaltite No. 1	171	176
Copper manganite No. 1	198	185
Cobalt aluminate No. 1	156	170
†Copper oxide No. 6	25	250

* Mr. C. G. Albert made the tests with nitrous oxide.

† 50 per cent oxidation.

REACTIONS OF COPPER OXIDE NO. 6

Some copper oxide No. 6 was put in a tube between two gas burets and heated to 370°C. Nitrous oxide was passed back and forth over it without any change in volume. Apparently it does not act as a catalyst for the dissociation of nitrous oxide. The fact that there is no free oxygen present in the nitrous oxide oxidation helps to account for the difference in temperature of equivalent conversions.

Hydrogen was passed over the catalyst at 175°C. Brownish copper-colored spots appeared on the catalyst at different places and the spots gradually spread out until the whole catalyst was copper colored. On exposure to the air the catalyst slowly turned to its original bluish green with a distinct evolution of heat. The catalytic activity was the same at the end of the experiment. This indicated that the copper oxide was so finely divided that the reduced copper was almost pyrophoric.

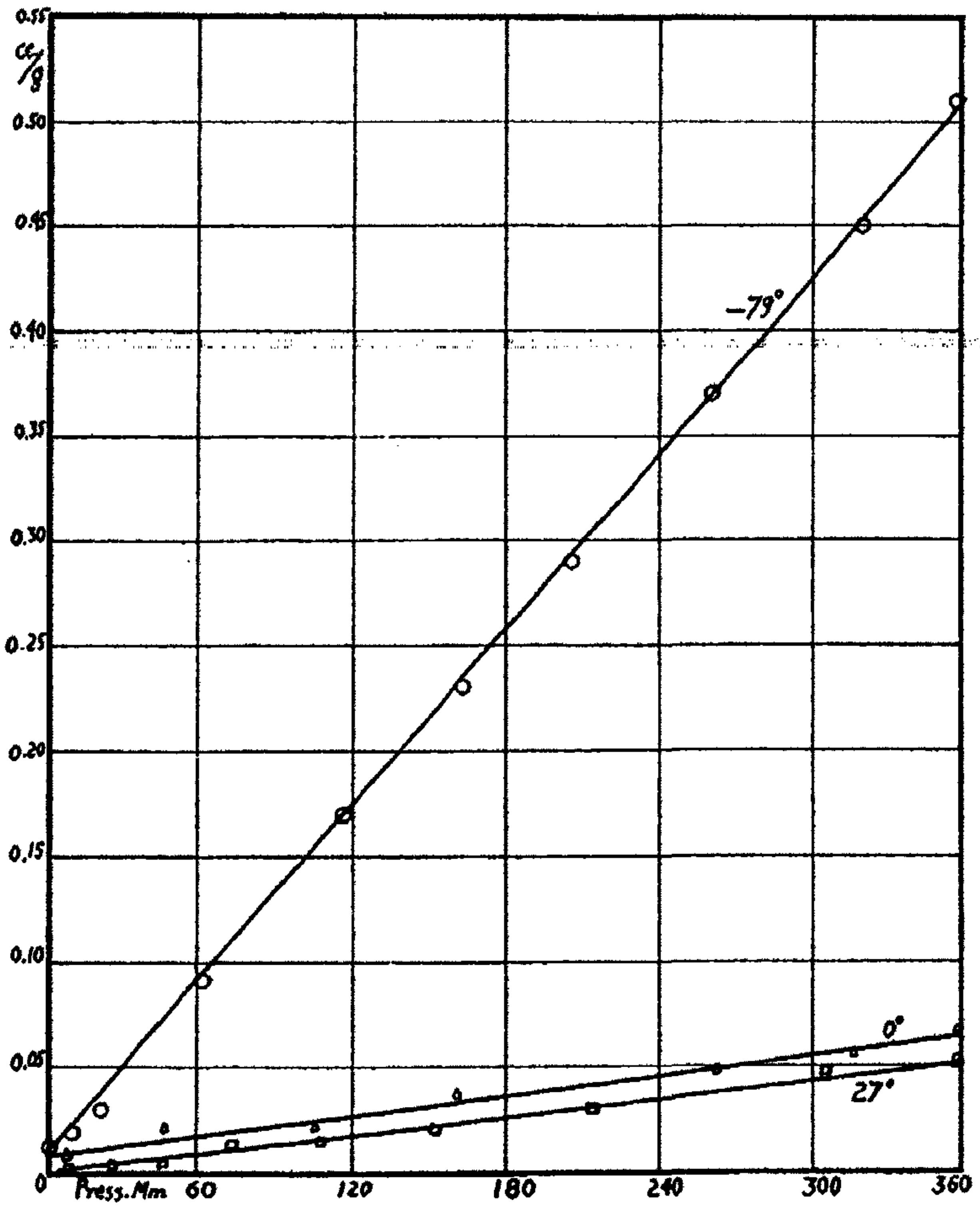

Fig. 1. Adsorption of Oxygen on Copper Oxide No. 6

Pure carbon monoxide was passed over the catalyst for 1.5 hours at 220°C., but no reduction was discernible, while hydrogen reduced the same catalyst completely in 10 minutes. Evidently an oxidation-reduction mechanism could not be used to explain the catalysis.

The adsorptive capacity of the catalyst for oxygen and for carbon monoxide was then determined. The adsorptions were made in the customary way. A mercury vapor pump was used to evacuate the apparatus to 10^{-5} cm. or better. The catalyst was degassed at 375°C. overnight after each run. The gases were purified by standard methods. The dead space in the apparatus was determined with helium. The sample of supported copper oxide weighed 6.33 g. and the dead space was 10.9 cc.

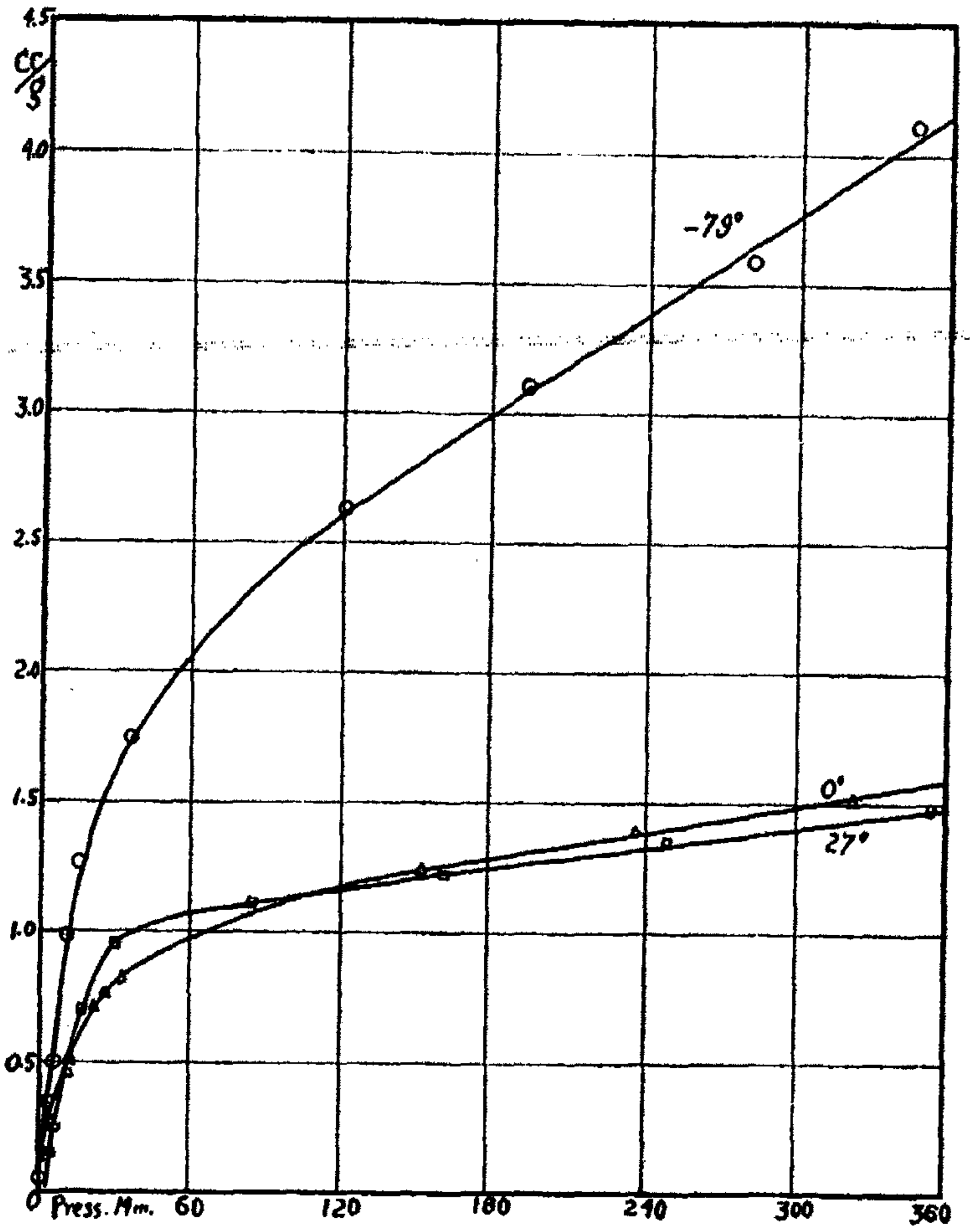

FIG. 2. ADSORPTION OF CARBON MONOXIDE ON COPPER OXIDE No. 6

The oxygen adsorption at all temperatures and pressures was instantaneous. The carbon monoxide adsorption was instantaneous at −79°C., but at 0°C. and room temperature there was an immediate adsorption followed by a slower adsorption which lasted from half an hour to four hours. The pressure decrease was rapid at first and then became progressively slower. This is indicative of chemical adsorption. The adsorption isotherms are shown in figures 1 and 2. The volume is calculated to standard conditions. They agree qualitatively with Benton's (4) adsorptions on copper oxide but show a larger adsorption, as would be expected from the more finely divided copper oxide. Adsorption measurements of oxygen, carbon monoxide, and carbon dioxide on copper chromite and other of the catalysts are now being made in this laboratory.

DISCUSSION OF RESULTS

From the standpoint of efficiency the supported copper oxide catalysts are by far the best of those reported, although several others give good conversion of carbon monoxide at moderate temperatures.

From the standpoint of the mechanism of the reaction it is possible to divide the catalysts into two groups,—those with a probable oxidation-reduction mechanism and those which probably do not have such a mechanism. The chromites, cobaltites, ferrites, and manganites may be put in the former class, while the aluminates and the supported copper oxides belong in the latter. It has been shown by Lory, and further substantiated by the present work, that there is a formation of surface chromate on the chromites and that this is reduced by carbon monoxide and oxidized by air and also nitrous oxide. These reactions indicate that the catalytic action is due to an alternate oxidation and reduction of the surface layer. The adsorption measurements being made here should throw further light on this.

On the other hand it appears that carbon monoxide will not reduce the copper oxide catalysts, and with the aluminates there is no possibility of valence change similar to that occurring with the chromites. The adsorption measurements show that carbon monoxide is chemically adsorbed on the surface of the copper oxide and also adsorbed very strongly, while the oxygen is adsorbed only slightly. Bone and Andrew (6) say that on ordinary copper oxide a layer of oxygen and nitrogen is adsorbed, that the oxygen is "activated," and that this oxygen oxidizes the carbon monoxide. However from the measurements made here it would seem that the carbon monoxide was the more strongly adsorbed and received an energy of activation due to adsorption and then reacted with the oxygen somewhat similarly to Langmuir's (21) explanation of the action of platinum on this same reaction.

SUMMARY

1. Methods of preparation and tests of eight chromite, six cobaltite, seven ferrite, four manganite, eleven aluminate, and six supported copper oxide catalysts have been given.

2. Further evidence has been advanced to show that the mechanism of the chromite catalysis is alternate oxidation and reduction.

3. The adsorption isotherms for oxygen and for carbon monoxide on a supported copper oxide catalyst at −79°C., 0°C., and 27°C. have been determined.

4. A mechanism for the catalytic action of the supported copper oxide catalysts has been proposed.

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SPECIFIC HEAT OF FURAN AND ETHYL ETHER VAPORS

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Received September 6, 1933

Inspection of the available data on the specific heats of gases and vapors reveals the fact that there has been very little experimental work published on the latter. This paper gives the results of investigations concerning the effect of temperature on the specific heat at substantially one atmosphere for the vapors of the two compounds, furan and ethyl ether. The data were obtained by the constant flow method and cover a temperature range of approximately 45°C. to 100°C.

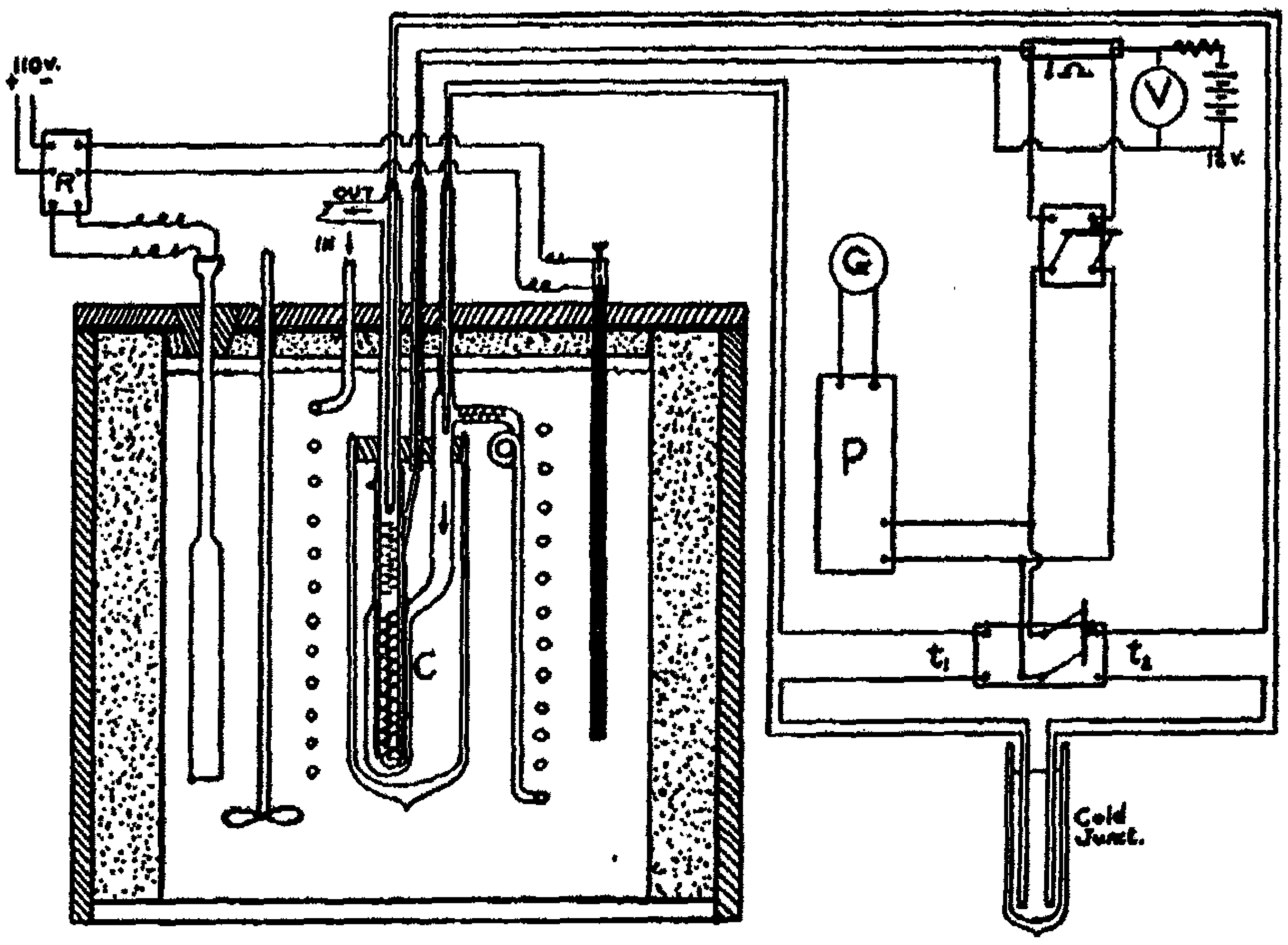

FIG. 1. FLOW CALORIMETER ASSEMBLY

Figure 1 gives the essential details of the apparatus. The design was essentially that used by Buffington and Fleischer (1). The oil bath was controlled to ±0.1°C. by a Cenco relay. In the case of calibration the volume of gas was measured on the outlet side by means of a specially designed Sprague gasometer which had been checked against a previously calibrated Sargent gas meter, the customary temperature and pressure corrections being made in every case. The ether and furan were vaporized from a brass boiler situated on a torsion balance, and recovered on the outlet side in a similar container immersed in an ice–salt mixture, with a vent to the atmosphere guarded by a calcium chloride tube. The boiler outlet tube was joined to the calorimeter inlet tube by means of a short rubber connection lined with tin foil. The boiler was wrapped with an insulated 110-volt heating coil, and various gas rates were obtained by adjustment of an external resistance in series with the heater. The inlet gas was brought to the temperature of the bath by passing through 8 meters of copper tubing immersed in the oil bath. The gas then passed over a 1-inch plug of copper gauze just before reaching the inlet thermocouple. The calorimeter proper was enclosed in a 500-cc. silvered Dewar flask immersed in the oil bath. The gas, after passing the inlet thermocouple, immediately entered the outer shell of the calorimeter proper, C, by way of two side-arm tubes. It then swept down the sides, over the heater leads, meeting the heating element at the bottom. The heating element consisted of a 75-ohm chromel "A" wire coil, supplied with current from lead storage cells, the amount of electrical energy being controlled by means of a slide wire resistance in series with the cells. The heater was enclosed in a double-walled, silvered Dewar tube, and provided with an insulated sheet metal radiation shield. After contact with the heater the gas passed over another plug of copper gauze just before reaching the outlet thermocouple. The thermocouples were made from No. 31 copper constantan wire and carefully calibrated over the range 0°C. to the boiling point of resublimed C.P. naphthalene. E.M.F. measurements were made with a Leeds and Northrup student's potentiometer, P, equipped with a Leeds and Northrup Type HS reflecting galvanometer, G. The voltage drop across the heater plus the standard 1-ohm resistance in series with it was measured by means of a voltmeter, V, checked against the potentiometer. The amount of current drawn by the heater was measured with the potentiometer from the drop in potential across the standard 1-ohm resistance. The electrical arrangement was designed to give continuous as well as accurate readings. The potentiometer was balanced against the standard cell before each run, and readings were taken over a period of twenty to thirty minutes after equilibrium had been reached. In the case of every gas, tests were made to ascertain the minimum gas rate above which the observed specific heat values were constant. For carbon dioxide this rate was found to be approximately 31 moles per hour, and for the other calibration gases approximately 35 moles per hour. For furan and ethyl ether the minimum gas rate proved to be 14 moles per hour.

A number of common gases including hydrogen, nitrogen, oxygen, carbon dioxide, and air were used for the purpose of calibration of the calorimeter. The hydrogen, nitrogen, and oxygen were of the laboratory grade as obtained from the Air Reduction Sales Co. The carbon dioxide was of a similar quality, obtained from Pure Carbonic, Incorp., Chicago, Illinois. All were passed over phosphorus pentoxide before entering the calorimeter. The compressed air was tapped off the laboratory supply and passed over soda lime, anhydrous calcium chloride, and finally phosphorus pentoxide. The furan was prepared according to the method of Gilman and Lousinian (4) by the decarboxylation of furoic acid in the presence of a tar base and copper oxide as catalyst, and refractionated over

TABLE 1

Flow calorimeter data and results for furan vapor at atmospheric pressure

RUN NO.	HEAT INPUT	VAPOR FLOW	TEMPERATURE RISE	C_p (CORRECTED)
		At 44.33°C.		
	cal. per hour	*g. per hour*	*degrees C.*	*cal. per mole per °C.*
1	533	1104	1.76	17.21
2	533	1146	1.69	17.29
3	533	1161	1.67	17.22
4	533	1020	1.91	17.17
5	533	1059	1.84	17.17
Average				17.21
		At 67.71°C.		
1	531	1275	1.40	18.67
2	390	1002	1.31	18.66
3	531	1092	1.64	18.61
4	531	1173	1.53	18.56
5	531	1146	1.57	18.53
Average				18.61
		At 98.99°C.		
1	529	1074	1.52	20.33
2	529	1110	1.48	20.21
3	530	1002	1.65	20.13
4	530	1143	1.44	20.21
5	530	984	1.65	20.49
6	527	1164	1.39	20.44
Average				20.30

anhydrous calcium chloride. Results of the sodium fusion test for nitrogen in the final product were negative. The ethyl ether used was of the Mallinckrodt C.P. anhydrous quality. All specific heat measurements were made on a middle fraction of each liquid. After completion of all measurements, the two liquids were redistilled. The boiling point ranges thus obtained were, for ethyl ether, 33.3°C. to 33.9°C., and for furan, 30.2°C. to 30.6°C., at 734.5 mm. The original calibration was then checked by a final run on hydrogen.

TABLE 2

Flow calorimeter data and results for ethyl ether vapor at atmospheric pressure

RUN NO.	HEAT INPUT	VAPOR FLOW	TEMPERATURE RISE	C_p (CORRECTED)
At 44.34°C.				
	cal. per hour	*g. per hour*	*degrees C.*	*cal. per mole per °C.*
1	882	1206	1.74	28.75
2	878	1350	1.55	28.66
3	878	1412	1.48	28.68
4	878	1514	1.37	28.80
5	878	1226	1.70	28.75
6	697	1150	1.44	28.75
Average				28.73
At 67.33°C.				
1	692	1329	1.17	30.45
2	872	1136	1.71	30.65
3	875	1384	1.42	30.37
4	1080	1420	1.69	30.64
5	875	1232	1.58	30.64
6	875	1288	1.51	30.74
Average				30.58
At 99.16°C.				
1	872	1496	1.24	32.13
2	872	1342	1.39	31.94
3	870	1188	1.56	32.06
4	872	1118	1.65	32.31
5	872	1308	1.41	32.29
6	873	1190	1.56	32.12
Average				32.14

Tests made on the Joule-Thomson coefficient proved it to be negligible.

A total of twenty-two calibration runs was made and the values compared with those calculated from the equations presented by Eastman (3). In all cases the calibration factor proved to be essentially a constant, 0.923. The values as found in tables 1 and 2 are believed to be accurate within 1 per cent for the temperature range covered by the measurements, 45°C. to 100°C., and may be represented by the following equations of the type employed by Eastman (3) and many other investigators, t being °C.: for furan vapor, $Cp = 14.2341 + 7.188 \times 10^{-2} t - 1.071 \times 10^{-4} t^2$; for ethyl ether vapor, $Cp = 23.3833 + 14.71 \times 10^{-2} t - 5.929 \times 10^{-4} t^2$. The data presented on furan vapor are the first to be published, and those on ethyl ether are believed to be the best available for the temperature range covered by the measurements.

Values for ethyl ether vapor calculated from the equation here presented compare with those found in the literature as follows, at 80°C., in calories per mole per °C.: Dixon and Greenwood (2), 27.81; Wiedemann (5), 32.66; authors, 31.36.

SUMMARY

The specific heat of furan vapor at atmospheric pressure was measured in a flow calorimeter at 44.33, 67.71 and 98.99°C., the data fitting the equation:

$$CP\ (\text{molal}) = 14.2341 + 7.188 \times 10^{-2} t - 1.071 \times 10^{-4} t^2\ (t\,°\text{C.})$$

Similar data on ethyl ether were found to fit the equation:

$$CP\ (\text{molal}) = 23.3833 + 14.71 \times 10^{-2} t - 5.929 \times 10^{-4} t^2\ (t\,°\text{C.})$$

The authors wish to thank R. M. Buffington for suggesting the general problem of the specific heats of polyatomic vapors. Thanks are also due Henry Gilman for supplying the relatively large quantity of furan used.

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THE FREE ENERGY OF FORMATION OF LEAD AMALGAMS[1,2]

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Received October 31, 1933

INTRODUCTION

The thermodynamic properties of the alloys of mercury with various metals have been carefully studied, particularly in the cases of thallium and cadmium. While a number of measurements of the electromotive force of lead amalgam cells have been made, there has been no systematic study of these systems.

Puschin (7) measured the potential of lead amalgams against lead in normal lead nitrate over the range from 92.6 to 1.8 atomic per cent of lead. From pure lead to 66 atomic per cent the amalgams are single-phase and solid; from 66 atomic per cent to 1.8 per cent, the lowest concentration measured, the amalgams are two-phase. The solid phase is lead mercuride, Pb_2Hg, while the liquid phase is a saturated solution in equilibrium with the solid. Puschin found a potential of 0.0063 volt at 20°C. for all the two-phase amalgams. Below about 1.4 atomic per cent of lead, the amalgams are unsaturated.

Gerke (4), Carmody (3), and Spencer (9) have measured the potential of lead against the saturated amalgams. Spencer's value is given by the equation $E = 0.00552 + 0.0000137t$, which gives 0.00586 at 25.00°C.

Babinski (1) has measured the potential of lead against unsaturated amalgams at several concentrations. Richards and Garrod-Thomas (8) have measured the potentials of concentration cells, covering the range from 1.02 atomic per cent of lead to an infinitely dilute amalgam.

In this article are presented the results of measurements on the potential of lead against unsaturated lead amalgams and against two-phase amalgams of higher lead content than those previously studied, together with the activities and free energies of formation calculated from them.

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[1] Contribution No. 275 from the Department of Chemistry, University of Pittsburgh.

[2] Submitted to the Graduate School of the University of Pittsburgh by Creig S. Hoyt in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

For this purpose, cells were prepared as follows:

$$\mathrm{Pb} \mid \mathrm{PbSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{PbSO_4} \mid \mathrm{PbHg_{satd.}}$$

and

$$\mathrm{PbHg_{satd.}} \mid \mathrm{PbSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{PbSO_4} \mid \mathrm{PbHg_{unsatd.}}$$

The chemical reaction occurring involves only the solution of lead in the amalgam in the first case and the transfer of lead from the more concentrated to the more dilute amalgam in the second. The zinc sulfate has no function save to decrease the internal resistance and thereby increase the sensitivity of the potential measurements.

PREPARATION OF MATERIALS

Lead

Lead for the amalgams and lead poles was Kahlbaum's "Lead for analysis" and gave the same potential as that prepared electrolytically. Lead electrodes were prepared by melting the freshly scraped bar, as furnished, under an atmosphere of hydrogen in a Pyrex tube and forcing the molten mass into a glass tube by the pressure of the hydrogen. The surface exposed to the electrolyte was scraped just before use. The platinum lead wire was cast in the electrode at the time of preparation.

Lead sulfate

Lead sulfate was prepared by precipitation from a solution of lead nitrate by zinc sulfate solution, according to the method of Bray (2), which is necessary to secure a reproducible potential at a lead-lead sulfate pole.

Mercury

Mercury was agitated with concentrated sulfuric acid and then distilled three times under diminished pressure according to the method of Hulett (5).

Lead amalgams

Lead amalgams were prepared by placing weighed amounts of mercury in a Pyrex separatory funnel with a capillary outlet. A rapid stream of hydrogen was introduced through an inlet tube sealed into the ground glass stopper, expelling the air from the flask through the outlet. Weighed amounts of lead sufficient to give lead amalgams of the desired concentrations were transferred to the funnels while the stream of hydrogen continued. The mixture was warmed and agitated until it was thoroughly homogeneous and then transferred to the cell while still at a temperature high enough to insure that a one-phase amalgam remained. The capillary outlet served to remove any oxide coating which might collect on the surface.

Amalgams, which were only homogeneous at high temperatures, were prepared in a Pyrex test tube with a capillary outlet under an atmosphere of hydrogen and allowed to flow into the cell while still liquid.

Nitrogen

Tank nitrogen was freed from oxygen by the method of van Brunt (11).

Preparation of the cells

The cells used were of the H type and made of Pyrex glass. A platinum lead wire was sealed into the base of each shank and into a mercury well through which connection could be made to the potentiometer. Glass tubes were inserted through stoppers in each arm, connecting with a Pyrex flask containing the electrolyte. A stream of nitrogen was bubbled through the electrolyte and thence through the cell for four hours. When a neutral atmosphere in the cell was insured, sufficient amalgam was introduced into the arm to cover the platinum lead. The electrolyte was then forced over from the flask into the cell by the pressure of the nitrogen. The glass outlet tubes were sealed to make the cell gas-tight and it was transferred to the thermostat containing kerosene and regulated to 0.02°C. The cells came to equilibrium in about twenty minutes and gave stable potentials for several hours. After this, cells with lead poles gave a slow but steady drift. Cells having both amalgam poles gave stable potentials for a somewhat longer time, but in ten to fifteen hours a gradual change in potential began and no steady value was subsequently obtained.

The potentials were measured with a Leeds and Northrup Type K potentiometer, well shielded, using a No. 2500-c galvanometer. The standard cell was calibrated by the Bureau of Standards.

RESULTS AND COMPUTATIONS

Free energy of formation of the amalgams

Teeter (10) has discussed a method for calculating the partial molal free energies of amalgams and, hence, the free energy of formation per mole of amalgam.

For the reaction represented by the equation, N_2 moles Pb(solid) + N_1 moles Hg(liquid) = Pb(amalgam, N_2), Hg(amalgam, N_1) + ΔF the free energy change may be calculated by the equation,

$$\Delta F = N_1 \Delta \bar{F}_1 + N_2 \Delta \bar{F}_2$$

where $\Delta\bar{F}^1$ and $\Delta\bar{F}_2$ are the partial molal free energies of transfer of mercury and lead, respectively, from the metallic state to amalgams of concentration

N_1, N_2. The partial molal free energies must be multiplied by the respective mole fractions, since these indicate the number of moles transferred.

Now

$$\Delta\bar{F}_1 = -NFE_1 = RT \ln a_1$$

where a_1 is the activity of mercury in the amalgam, and

$$\Delta\bar{F}_2 = -NFE_2$$

E_1 and E_2 are the potentials of the cells in which the transfer of mercury and lead from the respective metals to the amalgam occurs.

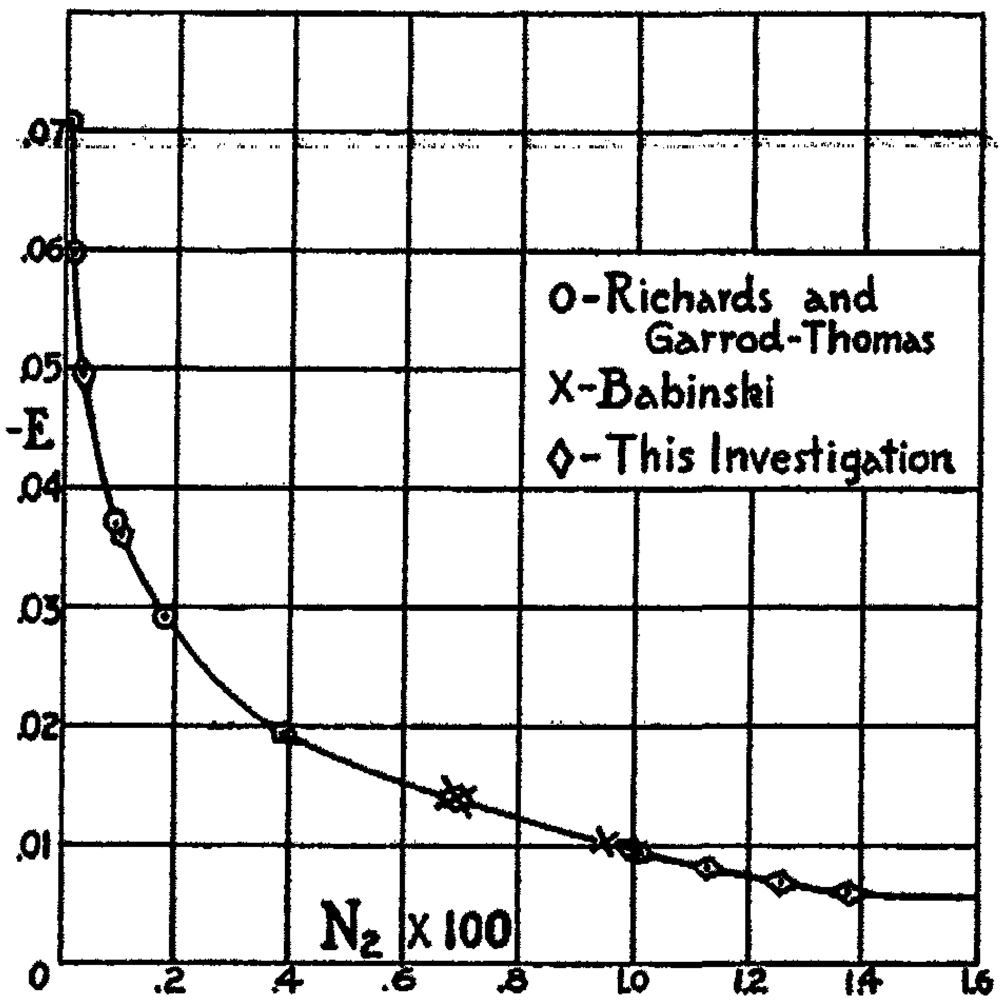

FIG. 1. E.M.F. OF LEAD AMALGAMS

The potentials of cells having the reaction

$$\text{Pb (solid)} = \text{Pb (amalgam, } N_2\text{)} + \Delta\bar{F}_2$$

for various values of N_2 have been determined by direct measurement and these have been plotted against the mole fraction of lead in figure 1.

By making a measurement of the electromotive force of one of the amalgams employed by Richards and Garrod-Thomas (8) against pure lead, the potentials of the amalgams employed in these concentration cells may be computed down to $N_2 = 0.000994$. By making the assumption that the activity coefficient of lead in the amalgams of Richards and Garrod-Thomas at $N_2 = 0.000994$ and 0.000932 are identical, the potentials of the entire series out to a mole fraction of 0.000068 may be calculated. These values have been plotted on the same curve and show good agreement with the present series of measurements.

Two measurements of Babinski (1) are available and these are plotted with the other data.

By extrapolating the curve to $-E = 0.00586$, the upper limit of concentration of the one-phase amalgam is found to be $N_2 = 0.0143$. Above this concentration, the amalgam consists of the compound, Pb_2Hg, and a saturated solution in equilibrium with it.

TABLE 1

Free energy of formation of one mole of lead amalgam

N_2	$-E_2$	a_2/N_2	a_1/N_1	$-N_2\Delta\bar{F}_2$	$-N_1\Delta\bar{F}_1$	$-\Delta F$
	volts			*joules*	*joules*	*joules*
0.000068	0.07082	0.990	0.999	0.928	0.00	0.928
0.000160	0.05982	0.995	0.999	1.846	0.406	2.252
0.000354	0.04980	0.975	0.999	3.614	0.850	4.464
0.00102	0.03648	0.946	0.999	7.392	2.530	9.922
0.00180	0.02924	0.935	0.999	10.158	4.615	14.773
0.00405	0.01957	0.879	0.999	15.294	10.640	25.934
0.00697	0.01401	0.785	0.998	19.008	19.453	38.461
0.00994	0.00993	0.754	0.998	19.05	28.03	47.08
0.0113	0.00834	0.750	0.997	18.19	28.21	46.40
0.0126	0.00724	0.732	0.997	17.60	30.95	48.55
0.0138	0.00629	0.720	0.996	16.75	34.26	51.01
0.0200	0.00586	—	0.993	22.62	65.05	87.67
0.0400	0.00586	—	0.972	45.24	161.37	206.61
0.0600	0.00586	—	0.953	67.86	255.70	323.56
0.0943	0.00586	—	0.883	106.6	501.9	608.5
0.1728	0.00584	—	0.807	195.4	830.0	1025.4
0.286	0.00582	—	0.707	323.5	1209.5	1533.0
0.443	0.00567	—	0.546	501.0	1642.7	2143.7
0.475	0.00584	—	0.517	538.4	1699.8	2238.2

$\Delta\bar{F}_2$ is calculated directly from the measurements of the potential of lead against the amalgams and, when multiplied by N_2, gives the partial molal free energy of lead per mole of amalgam.

$\Delta\bar{F}_1$, on the other hand, must be calculated from the equation, $\Delta\bar{F}_1 = RT \ln a_1$, since the standard state is pure mercury.

Lewis and Randall (6) have shown that the activity of a metal in an amalgam may be computed from the potential of the amalgam against an infinitely dilute amalgam, by plotting $(-E/0.02982 - \log N_2)$ against N_2, where the metal is bivalent, and extrapolating the curve to $N_2 = 0$. Since the infinitely dilute solution is chosen as the standard state, we have a_2/N_2

= 1, when N_2 equals 0, or log a_2/N_2 equals 0. By subtracting this value of the ordinate from the ordinate at any other value of N_2, we obtain log a_2/N_2 at that point. Table 1 gives the activities of lead calculated in this manner, from the most dilute amalgam measured by Richards and Garrod-Thomas to a saturated amalgam.

Lewis and Randall (6) have shown that the activity of mercury in the amalgam may be calculated by plotting $(-E/0.02982 - \log N_2)$ against N_2/N_1 and solving for log a_1/N_1 by graphical integration. Table 1 shows the activities of mercury in the amalgams and the partial molal free energy of mercury per mole of amalgam.

TABLE 2

Heat of solution of lead in amalgams at 25.00°C.

N_2	E	dE/dT	HEAT OF TRANSFER	HEAT OF SOLUTION
	mv.	mv.	joules	joules
0.000068 0.000160	11.00	0.03696	3.86	11,007
0.000160 0.000994	23.28	0.0792	64.45	11,003
0.000994 0.00180	8.13	0.0282	53.65	10,938
0.00180 0.00405	9.67	0.0334	54.58	10,885
0.00405 0.0102	9.94	0.0391	331.55	10,830
0.0102 0.0142	4.02	0.2016	10,824.3	10,499
0.0142 1.0000	5.86	0.0140	−325.4	−325.4

The partial molal free energies of transfer of lead and mercury, respectively, from the pure metal to the amalgam are multiplied by the mole fractions of the respective metals in the amalgam. The sum of these quantities is equal to the free energy of formation of one mole of amalgam.

In all amalgams in which N_2 is greater than 0.0143, the same solid phase is present and the values of a_1/N_1 and a_2/N_2 in the liquid phase are constant, regardless of the mole fraction of lead in the whole amalgam. So long as only the liquid phase is considered, these values are 0.996 and 0.717, respectively. When one mole of amalgam, consisting of both liquid and solid phases, is the basis, the activities change with the mole fraction.

Heat of solution of lead in lead amalgams

Richards and Garrod-Thomas (8) have determined the temperature coefficients of lead amalgam concentration cells between 0.00°C. and 29.96°C. The heat of transfer may be calculated from this data using the equation of Gibbs-Helmholtz.

$$-\Delta H = 192{,}988\,[E - T(\mathrm{d}E/\mathrm{d}T)]$$

where $T = 298.16$. Table 2 shows the heat of transfer of lead in lead amalgams and the heat of solution from an infinitely dilute amalgam to saturation.

SUMMARY

Concentration cells having pure lead as one pole and lead amalgams of varying concentration as the other have been constructed and their potentials measured. Reproducible potentials are secured with amalgams up to 66 atomic per cent of lead. The amalgam is saturated at 0.0142 mole fraction at 25.00°C. and all amalgams between that concentration and 0.66 give the same potential.

The free energy of formation of amalgams up to a mole fraction of approximately 0.50 have been calculated as well as the activities of lead and mercury in the amalgams.

The heat of solution of lead in unsaturated amalgams has been calculated from the temperature coefficient of the electromotive force.

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THE LATENT HEAT OF FUSION AND IDEAL SOLUBILITY OF NAPHTHALENE[1]

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Received October 12, 1933

In some previous work from this laboratory (8) it has been shown that the solubility of naphthalene in chlorobenzene exceeds the ideal solubility as calculated from the generally accepted value of the latent heat of fusion of the naphthalene by means of the Schröder (6) equation. This result is not to be expected on account of the relatively non-polar character of both substances. Moreover, a determination of the heat of fusion by Bogojawlenski (2) gave a value considerably lower than that accepted, and one which would give an ideal solubility more nearly in accord with that obtained in chlorobenzene. With the above exception, the earlier determinations as summarized by Mathews (4) give a latent heat of fusion per mole of 4560 calories. This is the value accepted by the International Critical Tables. Later determinations by Andrews, Lynn, and Johnston (1) and Spaght, Thomas, and Parks (7) give 4540 and 4585 calories, respectively. The former value is probably more reliable, but the authors do not claim an accuracy of more than ± 1 per cent. In view of the uncertainty it was deemed best to make a more accurate determination of the latent heat of fusion of naphthalene and especially to measure the heat capacities of the solid and liquid in order to determine the variation of the heat of fusion with the temperature and thus to fix the exact form of the ideal solubility curve.

EXPERIMENTAL

Materials

Naphthalene ("Baker's Analyzed") was recrystallized three times from methanol and further purified by fractional freezing twice. Neither method alone gave a pure product, but the combination gave a material that on freezing shrank in volume by about 20 per cent and formed an almost perfectly transparent solid which clung closely to the walls of the tube leaving a clean core in the center. The same freezing phenomena had been previously observed in the case of very pure benzene prepared by the

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[1] This work was made possible by assistance from a grant made by the Rockefeller Foundation to Washington University for research in science.

method of Richards and Shipley (5). The maximum amount of impurity which may be present in such materials is that which can form a saturated solid solution with the substance which freezes in the above manner, and perhaps a very slight amount which might be held in the interstices in the secondary or mosaic structure (10).

The melting point of the purified naphthalene was not less than 80.25°C. A sample from Kahlbaum and designated "for calorimetric purposes" showed the same melting point and was employed in a few determinations. The naphthalene was sealed up in soft glass tubes of about 9-mm. outside diameter and a wall thickness of about 0.5 mm. The total length of the tubes was about 18 cm. and the weight of naphthalene about 7 g.

The calorimeter

The container was a wide mouth Dewar flask of 1-liter capacity. This carried a closely fitting copper cover which extended on the outside about 3½ inches below the top of the calorimeter. The cover carried a small high speed turbine type of stirrer which revolved in a tube. There were also two holes with sliding covers for the admission of the sample and the thermometer, and a third very small hole for adjusting the level of the calorimetric liquid. The thermometer was of the platinum resistance type with a sensitive portion 10 cm. long and 1 cm. wide enclosed in a metal tube. It had been calibrated by the Bureau of Standards. A Mueller bridge was used to measure the resistance. Readings were made to 0.0001 ohm corresponding to about 0.001°C.

The calorimeter was clamped in the center of a 6-gallon earthenware jar filled with water until 2 inches of the calorimeter cover was immersed. The temperature of the water was regulated to ± 0.001°C. during the progress of the later calorimetric runs. To attain this constancy it was necessary to regulate the heating current and to stir violently with a large turbine type of stirrer. In some of the early determinations the regulation was to ± 0.01°C.

The calorimetric liquid was kerosene and the supply was kept constant by filling every day to a level exactly 3 cm. below the top of the cover. This adjustment was made by adding kerosene until the liquid rose in a small capillary tube at a calorimeter temperature of 22°C. The calorimeter was stirred at a constant rate of 1200 revolutions per minute by a small electric motor with a speed regulating device. The constancy of stirring during a run was tested by means of an A. C. neon light, applying the stroboscopic method to determine the rate of revolution of the pulley on the cover of the calorimeter. In a few of the earlier determinations the stirring rate was 1600 revolutions per minute and in others 1000 per minute.

The high temperature bath

This bath was made by winding a 1-inch round copper rod one foot long with nichrome ribbon, $\frac{1}{8}$ inch wide, No. 30 B & S, 0.43 ohm per foot. Thin asbestos sheet was placed between the ribbon and the rod, and the outside wound with several layers of sheet asbestos. The rod was bored from each end with a one-half inch hole and the upper end closed with a copper plug. Three and a half inches above the bottom of the furnace there was a small hole, through which a glass rod projected to hold the specimen in place. The temperature of the hot bath was determined by a single junction thermocouple constructed of No. 26 constantan and No. 28 copper wire. The hot junction was placed in a small hole bored parallel to the axis of the furnace and 4 inches deep. The electromotive force of the couple was measured by a Leeds and Northrup Type K potentiometer. The couple was calibrated in the same position in the furnace in which it was employed in the measurements. The standard instrument used for the comparison was a platinum resistance thermometer enclosed in glass, the sensitive portion being about 2 inches long. This portion was placed as nearly as possible in the position occupied by the specimen. Uniformity in this section was tested by raising and lowering the thermometer; the variation at 160°C. amounted to about 0.2°C. with a corresponding lower variation at the lower temperatures. It is estimated that the average temperature of the specimen under conditions of thermal equilibrium was known to less than 0.1°C., except possibly at temperatures above 130°C. In order to attain this accuracy it was necessary to heat with the current from storage batteries and to allow at least three hours from the start of the heating for the system to come to equilibrium. Even when changing the bath temperature but a few degrees, a 2-hour period was necessary for the temperature to become constant. It is probable that the greatest source of inaccuracy in the measurements was failure to attain equilibrium in the hot bath.

Calorimetric procedure

Before a run the temperature of the hot bath was read at intervals of five to ten minutes. When the temperature remained practically constant over such an interval, readings were made of the temperatures of the hot bath and the calorimeter on alternate minutes for a 10-minute rating period before the specimen was dropped into the calorimeter. After this, readings of the calorimetric temperatures were made during twenty minutes, for the first 2 minutes at half minute intervals and later every minute. The time intervals were observed on a stopclock which was started at the beginning of the run. The times between runs were in most cases sufficient to insure that the temperature of the calorimeter was not far from that of the bath at the start of the procedure. It was seldom that more than three runs could be made in a single day.

The temperature rise Δt was calculated from the formula, $\Delta t = \Theta_3 - \Theta_2 + \eta$, where Θ_3 is the temperature at the end of the 10-minute calorimetric period and Θ_2 that at the beginning of this period. The extrapolation correction, η, was calculated by means of the modification of the Regnault-Pfaundler formula due to White (9).

The calorimeter equivalent

Three materials were used as a basis for the measurement of this quantity. The first was a sample of parting silver of 99.95 per cent purity cast in a graphite mold. The sample weighed 53.5 g. The second was a bar of annealed electrolytic copper weighing 84 g., and the third 5.55 g. of water sealed in the same glass as was used to contain the naphthalene specimen. The heat capacities for the copper and silver were obtained from the International Critical Tables. When the determinations were made the same day, the calorimetric equivalent showed the same value for the different samples. For example, the temperature rise was 2.471×10^{-3} °C. per calorie for the silver sample, while the corresponding figures for copper and water were 2.473 and 2.473. Other determinations showed essentially the same agreement. There was, however, a considerable change in the calorimeter equivalent with the time. The highest value over a period of four months was 2.498 and the lowest 2.452. The maximum deviation from the mean of 2.475 was 0.9 per cent and the average 0.3 per cent. Certain causes of such deviations are slight variations in the amount of calorimetric liquid and the mending of the basket for holding the calorimetric specimen, but the most important was a change caused by two periods of abnormally cold weather. The equivalent rose rather rapidly during these periods and subsequently declined over a period of about a week. This change was probably due to the loss of moisture from the calorimeter, due to extremely low relative humidity. No change in the calorimetric equivalent was found when the temperature of the hot bath was changed. The above changes in the calorimeter equivalent made necessary the determination of its value on practically every day upon which a run was made, especially in the case of the liquid naphthalene. The metal, usually copper, was heated to nearly the same temperature as that employed for the naphthalene or glass samples.

THE EXPERIMENTAL RESULTS

All the observations on naphthalene were reduced to a common calorimeter equivalent of 2.470×10^{-3} °C. per calorie and to a basic temperature of 22°C. Correction was then made for the glass which enclosed the specimen from a large scale curve drawn for that substance. The experimental results were then plotted on a large scale, curves were drawn, and their equations calculated. The experimental results appear in tables 1 and 2.

TABLE 1

Molal heat content for solid naphthalene reckoned from a basic temperature of 22°C.

TEMPERATURE	H_s (OBSERVED)	Δ	TEMPERATURE	H_s (OBSERVED)	Δ
degrees C.	*calories per mole*		*degrees C.*	*calories per mole*	
36.67	588	0	74.21	2291	+24*
48.79	1006	+6	76.35	2375	+2
59.61	1563	−12	76.51	2412	+32†
65.48	1874	+26	76.69	2351	−38
66.41	1881	−10	77.08	2399	−10
68.33	1988	+13	77.37	2412	−11
69.28	2033	+4	79.50	2552	+18
72.58	2192	+4*	79.90	2750	+200

* Kahlbaum's naphthalene (for calorimetric purposes).
† Bath stirring irregular.

TABLE 2

Molal heat content of liquid naphthalene reckoned from a basic temperature of 22°C.

TEMPERATURE	H_l (OBSERVED)	Δ	TEMPERATURE	H_l (OBSERVED)	Δ
degrees C.	*calories per mole*		*degrees C.*	*calories per mole*	
70.03	6550	+5	99.38	8062	+3
74.16	6755	+4	100.11	8030	−67‡
75.53	6825	+5	102.96	8230	−20
76.24	6863	+5	107.95	8480	−42
76.51	6863	−7	108.54	8540	−12
79.75	7050	+15	114.50	8865	−13
79.79	7025	−13	124.75	9460	+17
80.43	7058	−14*	128.46	9640	−12
81.09	7147	+42*	136.50	10150	+43*
81.77	7145	+6	137.86	10190	+2
84.00	7195	−59†	143.74	10510	−19
86.91	7370	+7	150.25	10920	+14
87.68	7460	+41	160.41	11515	+2
89.46	7520	−19	161.80	11560	−34
95.29	7840	−5	172.82	12210	−48

* Kahlbaum's naphthalene (for calorimetric purposes).
† Irregularity in calorimetric equivalent.
‡ Bath temperature not constant.

All observations made after a certain date are included except two or three for which a very definite reason for rejection could be assigned. The determinations on liquid naphthalene below 80°C. were made by first heating the specimen above 90°C. for a considerable time and then cooling in the furnace until temperature equilibrium was reached. The sample of naphthalene from Kahlbaum did not supercool to any extent, but on fractional freezing behaved as regards supercooling in the same manner as did the highly purified material employed in most of the calorimetric determinations.

The values under the heading Δ in the tables indicate the deviations of the experimental results from the empirical curves employed to express the variation in the molal heat content with the temperature. The equations employed are $H_s = -781 + 33.17\,t + 0.1068t^2$ calories per mole for the solid, and $H_l = 3309 + 42.4t + 0.0546t^2$ calories per mole for the liquid, both values being calculated from a basic temperature of 22°C. The symbol t denotes the centigrade temperature.

The latent heat of fusion of naphthalene

When the equation for the heat content value for the solid is subtracted from that for the liquid, an expression is obtained for the value of the molal heat of fusion of naphthalene at various temperatures, at and below the melting point. The equation obtained is $\Delta H_f = 4090 + 9.23t - 0.0522t^2$. This indicates a value of the latent heat of fusion at 80°C. of 4495 calories per mole. The value at 70°C. is 4480 calories and at 50°C. this has fallen to 4420 calories. The results show a smaller variation of the latent heat of fusion with the temperature than is the case for most organic substances. In the list studied by Andrews, Lynn, and Johnston (1) only quinone and the aminobenzoic acids had smaller differences in the heat capacities of the solid and liquid substances at the melting point. In the latter substances the results were unsatisfactory owing to decomposition.

The ideal solubility of naphthalene

Lewis (3) defines an ideal solution as one that obeys Raoult's law at all temperatures and pressures, and shows that the formation of such a solution will take place from its component liquids without any heat of mixing or change in volume. This means for the ideal solution of a solid in a liquid that the heat of mixing shall be the heat of fusion of the solid at the temperature at which the solution is made. On this basis the ideal solubility may be calculated by means of a modification of the Schröder (6) equation which takes into account the variation in the latent heat of fusion with the temperature. The equation expressing this variation as given above is transformed into absolute temperatures giving $\Delta H_f = -2375 + 38.10T - 0.0528T^2$. This expression is not, of course, valid at temperatures much below 0°C. The above value is substituted in the equation

$$\frac{d \ln N}{dT} = \frac{\Delta H_f}{RT^2}$$

and integration gives

$$\ln N = 1195\left(\frac{1}{T} - \frac{1}{T_m}\right) - 19.17 \ln \frac{T_m}{T} + 0.02657(T_m - T)$$

where T_m is the absolute melting point of the naphthalene. In table 3 appear the values of the ideal solubility, expressed in mole fraction of naphthalene, as calculated by means of the above expression. The second column gives the results obtained when 353.4° was used as the absolute melting point of the naphthalene. This figure is probably within 0.05° of the melting point of perfectly pure naphthalene. Since in the investigation of the solubility of naphthalene (8) a material of an absolute melting point of 353.15° was employed, the ideal solubility was recalculated on that basis and the results appear in the third column. The experimental and interpolated values for the mole fraction of naphthalene when forming a saturated solution in chlorobenzene at various temperatures are shown in the fourth column. The values at the rounded temperatures are the interpolated values, while the others are the experimentally observed points from which the rounded values were obtained by graphic interpolation. These values are taken directly from the previous publication (8). In the last column of the table appear the values for the ideal solubility as calculated by the original form of the Schröder equation, using 4495 calories as the molal heat of fusion of naphthalene.

TABLE 3

The ideal solubility of naphthalene

TEMPERATURE	MOLE FRACTION OF NAPHTHALENE $T_m = 353.4$	MOLE FRACTION OF NAPHTHALENE $T_m = 353.15$	MOLE FRACTION OF NAPHTHALENE SATURATED SOLUTION IN CHLOROBENZENE	MOLE FRACTION OF NAPHTHALENE ΔH_f CONSTANT AT 4495 CALORIES PER MOLE
degrees C.				
70	0.819	0.828	0.830	0.829
62.6	0.714	0.716	0.716	0.717
60.0	0.678	0.681	0.682	0.680
50.0	0.551	0.553	0.555	0.551
49.0	0.540	0.541	0.540	0.540
42.8	0.471	0.473	0.473	0.470
40.0	0.442	0.444	0.444	0.441
30.0	0.351	0.352	0.352	0.348
29.4	0.346	0.347	0.349	0.342
22.1	0.290	0.291	0.292	0.285
20.0	0.275	0.277	0.277	0.269
10.0	0.213	0.214	0.215	0.205
8.8	0.207	0.207	0.208	0.198
4.2	0.183	0.183	0.185	0.174
0.0	0.163	0.163		

DISCUSSION

The value of the latent heat of fusion of naphthalene obtained in this investigation is about 1 per cent lower than the value found by Andrews, Lynn, and Johnston (1). A large part of the discrepancy can be accounted for by the fact that those investigators used the straight extrapolation method for obtaining the calorimetric temperature rise, while in this investigation a more exact modification of the Regnault-Pfaundler formula has been employed. In the determination of the calorimetric equivalent, under the conditions employed in this work, the two methods give almost identical results, but with the naphthalene the simple extrapolation gave considerably higher values for the reason that the heat was developed quite slowly at the beginning of the calorimetric period even though the time at which the fall of temperature became regular differed but little from the corresponding time for the copper sample. In one measurement for the liquid naphthalene at about 80°C. and the corresponding determination of the calorimeter equivalent, the extrapolation method gave a heat content per mole 45 calories higher than that obtained by the more exact method. For the solid naphthalene the heat exchange with the calorimeter was more rapid than for the copper sample at the same temperature. In this instance, therefore, the method of calculation would account for the difference between the results of Andrews, Lynn, and Johnston and those reported in this paper.

The measurement of the heat content of the supercooled liquid naphthalene is not important for the measurement of the variation of the latent heat of fusion with the temperature, since this variation is small and the degree of supercooling attained was not very great, but it does give a much greater certainty in obtaining the latent heat of fusion at the melting points, since the interpolation errors in the heat content curve for the liquid are considerably less than the extrapolation errors. The extrapolation errors in the heat content curve for the solid should be small numerically, since the extrapolation is carried over a short distance and the heat content is small. It is believed that a value for the latent heat of fusion of naphthalene of 4495 calories is accurate to within ± 15 calories.

It might be argued that a very long extrapolation of the heat content curve for the liquid is necessary to obtain the latent heat of fusion at the lower temperatures; this criticism is doubtless justified, but it is to be noted that the ideal solubility as calculated from an invariant heat of fusion does not differ appreciably from that taking into account such variation until a temperature at least thirty degrees below the melting point is reached. Even at the lower temperatures the discrepancies are not great and the correction introduced by employing the more exact formula is in the right direction and of the right order of magnitude to bring the ideal solubility into close agreement with the observed solubility of naphthalene in chlorobenzene.

SUMMARY

1. Very pure naphthalene having a melting point of 80.25–80.3°C. has been prepared and some interesting phenomena on its freezing have been noted.

2. The latent heat of fusion of this material has been found to be 4495 calories per mole.

3. A reason has been suggested to account for the fact that this value is somewhat lower than the usually accepted value.

4. The ideal solubility of naphthalene has been calculated by a method which takes into account the variation in the latent heat of fusion with the temperature. The results show excellent agreement with previously published data on the solubility of naphthalene in chlorobenzene.

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THE DIFFUSION OF ELECTROLYTES IN SILICA GEL[1]

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Received July 25, 1933

INTRODUCTION

The purpose of this paper is to give quantitative methods for the preparation of impregnated gels of silica, and to explain the anomalous effect of high acid concentration on the washing of such gels. The first portion of the paper deals with the preparation of impregnated gels; the second with the measurements of the diffusion rates of acid and salts in silica gel. The results of the diffusion measurements give an explanation of the behavior of the impregnated gels during dialysis.

EXPERIMENTAL I

Analyses of material

In the preparation of silica gels, it is important to know the concentration of the sodium oxide and of the silicon dioxide, and the ratio of these two in the water glass in order to duplicate the preparations. This information is often absent from papers dealing with the formation of such gels. The analysis of the water glass used in our experiments is as follows: $NaOH = 3.56$ molar; $SiO_2 = 6.67$ molar; ratio SiO_2 to $Na_2O = 3.75$.

Preparation of the gels

The method used for the formation of the gels impregnated with heavy metal salts is similar to that of Klosky and Patrick (1). A measured volume of a salt of known concentration was added to a definite amount of 10 normal hydrochloric acid solution. Various volumes of standard sodium silicate solution were then added to this salt–acid mixture. The combinations employed are shown in table 1.

General method for preparation of impregnated gels of silica

As the presence of the salt has but little effect on the sol–gel transformation, a good gel containing any of the above salts may be obtained in the

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[1] From the dissertation submitted by B. W. Allan to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1932.

following manner. To 30 cc. of 10 *N* hydrochloric acid and 10 cc. of any of the salts used above, add with constant stirring 100 cc. of 1 per cent sodium silicate solution. The rigidity of the gels may be increased by using a more concentrated solution of water glass. These gels should then be washed until acid-free.

Behavior of the gels on washing

After the impregnated gels were successfully prepared, it was decided to determine quantitatively the loss of heavy metal ion during dialysis. Two gels impregnated with ferric chloride were prepared. One contained a small amount of acid, the other a large amount. Two gels containing copper chloride were prepared in a similar manner. These gels were carefully analyzed before and after sixty hours of dialysis. The results are given briefly in table 2.

TABLE 1

Preparation of gels impregnated with heavy metal salts

NO.	SALT SOLUTION		HYDROCHLORIC ACID 10 *N*	SODIUM SILICATE 1 PER CENT	REMARKS
	Concentration	Volume added			
Iron gel					
		cc.	*cc.*	*cc.*	
1	0.1930 g. $FeCl_3$ per cc.	5.0	2.5	100	Clear sol; no gel in two weeks
2		5.0	3.0	100	Clear sol; no gel in two weeks
3		5.0	6.0	100	Clear sol; gel in one week
4		5.0	4.5	25	Clear sol; perfect gel in two hours
Copper gel					
1	0.2438 g. $CuCl_2$ per cc.	5.0	5.0	100	Clear sol; no gel in one week
2		5.0	3.0	100	Precipitate
3		5.0	5.0	70	Clear sol; soft gel in one week
4		5.0	5.0	30	Clear sol; gel in two hours
Manganese gel					
1	0.2148 g. $MnCl_2$ per cc.	5.0	4.0	100	Clear sol; no gel in one week
2		5.0	5.0	100	Clear sol; no gel in one week
3		5.0	5.0	90	Clear sol; gel in one week
4		5.0	5.0	30	Clear sol; gel in three hours

Two important facts were obtained from these analyses. Salts which are easily hydrolyzed are retained more strongly than those which are not, and salts are held more tenaciously by gels which contain a large excess of acid.

EXPERIMENTAL II

It is obvious that experiments like those described above are laborious and time-consuming; therefore it was desirable to attack the problem in another manner. Plans were now undertaken to measure the rate of diffusion of salts and acid through pure silica gel. However, none of the orthodox methods for measuring diffusion rates is applicable to silicic acid gel, owing to its shrinkage during syneresis and to its lack of adhesion to glass.

Finally it was decided to prepare permanent discs of silicic acid, and to measure diffusion through them. A mold was made from which thirty-six discs, 2.60 cm. in diameter and 1.90 cm. in thickness, could be made at once. These discs were made by preparing a sol of silicic acid which was then poured into the mold and allowed to set until gelation had occurred. They were then removed, dialyzed, and allowed to dry in the air several days. Of course the discs shrunk on drying. When they had decreased to a definite size, they were replaced in water. However after the gel discs had lost such a large amount of water, it was impossible to replace them in water without their cracking to pieces. This was due to surface strains brought about by the unequal absorption of water. By preparing a gel of low acid content this difficulty was overcome. The properties of this gel were superior to any of those previously prepared. The discs could be dried readily without breakage. A stream of water-laden air was passed over them in order to resaturate them gradually. After this treatment they could be replaced in water without any danger of breakage. On drying, all the discs did not shrink to the same size. Since only six discs were needed these could be selected with ease from the lot.

TABLE 2

Behavior of the gels on washing

GEL	SAMPLE	EXCESS ACID PER 100 CC. HYDROGEL	RATIO $\frac{\text{MOLES SiO}_2}{\text{MOLES Fe}}$	RATIO $\frac{\text{MOLES SiO}_2}{\text{MOLES Cu}}$
		moles		
Iron	Original gel	0.0173	6.94:1	
	Washed gel	0.0000	17.35:1	
	Original gel	0.4025	6.94:1	
	Washed gel	0.0000	16.69:1	
Copper	Original gel	0.0173		6.31:1
	Washed gel	0.0000		247.00:1
	Original gel	0.4025		6.31:1
	Washed gel	0.0000		151.62:1

Figure 1 shows the apparatus in which the discs were employed. A series of such apparatus was arranged in a large air-bath thermostat which was kept at a constant temperature of 32.50°C. A 20-liter aspirator bottle on the top of the thermostat acted as a distilled water reservoir. This was connected by glass tubing to a smaller aspirator bottle (2-liter) inside the thermostat. The small reservoir was so constructed that the water drawn from it was always under a constant pressure and temperature. A large tube (1.5 cm. in diameter) from which side arms protruded carried water from the small reservoir to each of the diffusion cells. These side tubes entered the inlet tube of the cell. By means of stopcocks the flow of distilled water through these cells could be regulated. The rubber tubing in which the discs were held was attached to the reservoirs which were used to hold the salt solution. These salt reservoirs could easily be adjusted so that the face of the disc came in contact with the distilled water which flowed through the cell. After the salt reservoirs had been charged, the flow of water through the cells was regulated. The salt solutions were

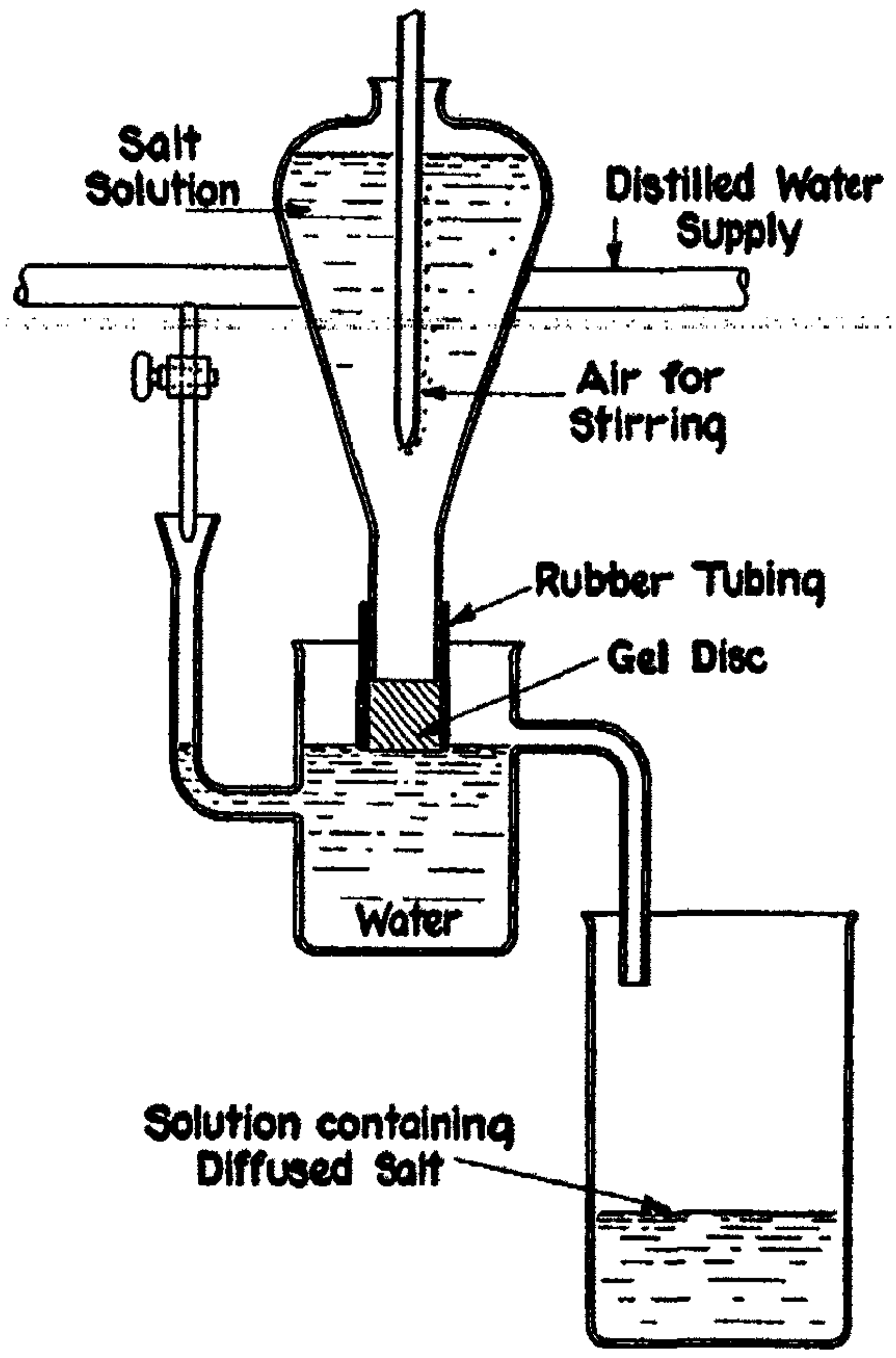

FIG. 1. APPARATUS USED IN MAKING THE MEASUREMENTS

stirred by bubbling air through them. This air had previously been saturated with moisture to prevent evaporation of the solvent from the salt solutions. Preliminary runs proved to be entirely satisfactory.

Measurements

The reservoirs were charged with their salt solution and the apparatus was adjusted and allowed to come to equilibrium. That is, diffusion was allowed to take place until the amount of solute passing through these discs per unit of time was constant. After this so-called "steady state" was reached, the liquid was removed from the cells, which were then thoroughly rinsed with distilled water. The flow of water through these cells was adjusted to the rate of 20 cc. per hour. Clean 800-cc. beakers were placed under each cell to catch the solution which flowed out of them. The thermostat was closed and the time recorded. After a definite time, approximately twenty-four hours, the run was discontinued. The solutions in the cells were removed and put in the beakers which had been placed under them. The cells were flushed out and this solution was added to that already in the beakers.

TABLE 3

Results of the first run

NO.	SALT USED	ACID USED	CONCENTRATION OF SALT	CONCENTRATION OF ACID	TIME OF RUN	$NaOH$	$AgNO_3$	$NaOH$ IN TERMS OF $AgNO_3$	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-4}$
			N	*N*	*hours*	*cc.*			
1	LiCl	None	0.90	0	24	0	3.60		1.796
2	NaCl	None	0.90	0	24	0	6.40		3.193
3	KCl	None	0.90	0	24	0	8.95		4.470
4	LiCl	HCl	0.90	1.15	24	10.30	19.95	18.45	0.749
5	NaCl	HCl	0.90	1.15	24	12.80	25.50	22.95	1.273
6	KCl	HCl	0.90	1.15	24	13.30	27.55	23.80	1.872

TABLE 4

Average values of three runs

NO.	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-4}$	DIFFUSION COEFFICIENT $\times 10^{-6}$
1	1.788	1.92
2	3.202	3.43
3	4.390	4.69
4	0.736	0.79
5	1.313	1.41
6	1.948	2.08

The salts used in these first measurements were lithium, sodium, and potassium chlorides; the acid was hydrochloric acid. The amount of diffusion was measured by analyzing the amount of salt and acid which came through the disc per unit of time. The amount of salt was determined by the method of Mohr, assuming that the concentration of the chloride ion gave a measure of the amount of salt present. Of course, in those experiments where both acid and salt were used, the concentration of the hydrochloric acid was first determined, then the total chloride concentration. Obviously, the difference gave the amount of salt. Since the end points in these titrations are hard to observe, all the solutions were concentrated to a small volume and actual titrations were done in artificial illumination. Also a blank was run before each series of analyses. The results of the experiments are given in tables 3 and 4.

TABLE 5

The effect of different salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (*M*)	NaOH (AVERAGE OF 3 RUNS)	DIFFUSION COEFFICENT (AVERAGE OF 3 RUNS)
		molar			
1	None	0	1.15	11.23	8.61×10^{-6}
2	$CuCl_2$	0.3165	1.15	12.18	9.33×10^{-6}
3	$FeCl_3$	0.2782	1.15	11.48	8.81×10^{-6}
4	LiCl	0.9000	1.15	16.03	12.21×10^{-6}
5	NaCl	0.9000	1.15	16.80	12.78×10^{-6}
6	KCl	0.9000	1.15	16.15	12.38×10^{-6}

TABLE 6

The effect of salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (*M*)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		molar			
1	None	0	1.150	11.01	8.43×10^{-6}
2	$CuCl_2$	0.6335	1.150	13.97	10.71×10^{-6}
3	$FeCl_3$	0.5564	1.150	11.93	9.15×10^{-6}
4	LiCl	1.800	1.150	19.90	15.24×10^{-6}
5	NaCl	1.800	1.150	20.98	16.29×10^{-6}
6	KCl	1.800	1.150	20.02	15.37×10^{-6}

The discs employed had the following dimensions: diameter, 1.18 cm.; thickness, 0.91 cm.; area of face, 1.094 cm.^{2} The temperature of the thermostat was 32.50°C. Three such series of runs were made. The results in table 4 are average values of three runs.

It is seen from the results given in tables 3 and 4 that the order of the diffusion coefficient is as follows: K > Na > Li. It is also shown that the diffusion coefficients of the salts are greatly affected by the presence of the acid. In each case the diffusion rate of each salt is diminished by the presence of acid.

Runs were now made to ascertain the effect of different salts on the rate of diffusion of hydrochloric acid. The discs employed had the following dimensions: diameter, 1.16 cm.; thickness, 0.90 cm.; area of face, 1.058 cm.^{2} The time of each run was 24 hours. The results are given in table 5.

The concentrations of the salts were increased. The time of each run was 24 hours. The results are shown in table 6.

Table 7 gives the results obtained on increasing the concentration of the ferric and cupric chlorides.

The results of these experiments are plainly visible. The diffusion rate of the hydrochloric acid was increased by the presence of salts.

TABLE 7

The effect of salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (*N*)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		molar			
1	None	0	1.150	11.10	8.52×10^{-6}
2	$CuCl_2$	1.00	1.150	16.98	13.00×10^{-6}
3	$FeCl_3$	1.00	1.150	14.92	11.43×10^{-6}

DISCUSSION

According to the Nernst theory of diffusion, which leads to the elementary explanation of the liquid potential, a mobile ion should increase the rate of diffusion of a more slowly moving oppositely charged ion. Furthermore, in the case of mixed electrolytes the more mobile ion will be retarded by the other ions, which in turn will experience an increase in mobility. This simple theory has been found to be in agreement with much experimental fact when dealing with ordinary diffusion phenomena. However, in the case of diffusion from a solution through a rigid gel structure, the above explanation no longer holds. Our washing of impregnated gels showed a marked retardation of the diffusion of the salt in the presence of acid, while our diffusion experiments through silica gel discs not only definitely proved the same point, but we were also able to show that the diffusion of the acid was speeded up in the presence of salt. These facts are in conflict with the Nernst theory; incidentally, Nernst never applied his ideas to systems such as used in this study.

One of the authors of this paper has recently developed a comprehensive theory which promises a satisfactory explanation of all the experimental findings. Inasmuch as the development of the theory involves the discussion of much unpublished experimental work, it is thought inadvisable to attempt the argument at this time. Suffice it to say that it centers around an electrokinetic potential at the gel-solution interface.

SUMMARY

1. Quantitative methods have been worked out for the preparation of impregnated gels of silicic acid.

2. The anomalous effect of acid on the washing of such gels has been observed and an explanation has been advanced to account for the behavior.

3. Methods of preparing discs of silica gel, which permit the drying of such discs without shattering, have been discovered.

4. The diffusion of salts and acids has been studied in hydrated silica gel.

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SURFACE TENSION AND MOLECULAR VOLUME OF NITROGLYCERINE

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Received January 5, 1934

These measurements have been made in connection with the theory that the sensitivity of an explosive is associated with a state of "strain" within its molecule. An examination of the meagre results available hitherto gave some support to the theory, in that the value of the parachor appeared to be abnormal; no support, however, is given by the more carefully determined values that have now been obtained for the typical liquid explosive, nitroglycerine (glyceryl trinitrate).

PURITY OF SAMPLE

As received from the factory,[1] the nitroglycerine was absorbed in kieselguhr. It was recovered by displacement with water and was subsequently filtered through glass wool and muslin.

The composition was checked by measurement of the refractive index and the nitrogen content; the sample was thus shown to be free from detectable amounts of water and of glyceryl dinitrate.

The further examination was confined to the following overall test of the effect on surface tension of traces of impurities rather than to a detailed estimation of the amount of each impurity.

Effect of impurities

Impurities in a liquid are drawn into or away from the surface layer according as their presence lowers or raises the surface energy. In the former case, the lowering is disproportionately great, and a trace of impurity may produce an appreciable effect. A method of detecting this effect has therefore been devised on the following lines.

The effect is less pronounced with the freshly formed surface of a growing bubble than with a stationary surface confined in a capillary tube. In addition, therefore to measuring the surface tension by Sugden's (3) bubble-pressure method, measurements have been made by the capillary methods of Ferguson and Kennedy (1) and of Sutton (4). These capillary methods were designed for use when very little material is avail-

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[1] Royal Gunpowder Factory, Waltham Abbey.

able, and are not as sensitive as the Sugden method; for the present purpose, however, they have the advantage that any error in the Sugden value due to impurity is magnified and detected.

Table 1 gives a series of values obtained with two samples of nitroglycerine insufficiently purified and a sample from the same source after further filtering and drying.

TABLE 1

Effect of impurities

SAMPLE	SURFACE TENSION MEASURED BY METHOD OF			REMARKS
	Sugden (3)	Ferguson and Kennedy (1)	Sutton (4)	
	dynes per cm.	*dynes per cm.*	*dynes per cm.*	
I	49.$_8$	45	42	After preliminary drying and filtering. Sample rejected
II	49.$_1$	43	38	After preliminary drying and filtering. Sample rejected
III	50.$_3$	50	51	Sample from same source as II. After further drying and filtering

TABLE 2

Parachor of nitroglycerine

TEMPERATURE	SURFACE TENSION	DENSITY	PARACHOR		METHOD OF MEASUREMENT
degrees C.	*dynes per cm.*				
20.5	50.4	1.595	379.$_3$		Sugden
20.5	50.1	1.595	378.$_7$		Sugden
16.5	51.1	1.599	379.$_6$	mean	Sugden
16.7	50.8	1.599	379.$_1$	379.3	Sugden
21.5	50.3	1.594	379.$_4$		Sugden
21.5	50.3	1.594	379.$_4$		Sugden
22.0	50.$_2$	1.593	379		Ferguson
20.0	51.$_1$	1.595	380		Sutton
20.1	50.$_4$	1.595	379		Ferguson
17.2	51.$_4$	1.599	380		Sutton
18.1	50.$_2$	1.598	378		Ferguson
18.0	49.$_9$	1.598	378		Ferguson

The effect of residual impurities is conspicuously greater when the Sutton or the Ferguson and Kennedy method is used. Agreement between the three methods is taken as an indication that the purity is adequate and the Sugden value is that given by pure nitroglycerine.

RESULTS

The measured values of the surface tension, the measured densities, and the values of the parachor derived from these are given in table 2. The agreement of the values obtained by the Sugden bubble-pressure method with those obtained by the capillary methods of Sutton and of Ferguson and Kennedy shows (see above) that the purity of the sample was adequate. The value found for the parachor, 379.3, may be compared with the value 378.9 which is obtained from the standard constants deduced by Sugden for carbon, hydrogen, oxygen, and the nitro group.

TABLE 3

"Parachor" of nitroglycerine-nitrobenzene solutions

I		II	III	IV	V	VI	VII
MOLAR COMPOSITION		TEMPERATURE	SURFACE TENSION	DENSITY	"PARACHOR" OF SOLUTION (Calculated from Columns III and IV)	"PARACHOR" OF SOLUTION (Calculated from parachors of nitroglycerine and nitrobenzene)	DIFFERENCE
Nitrobenzene	Nitroglycerine						
		degrees C.	*dynes per cm*				
100.0	0.0					264.3	
84.5	15.5	20.0	43.6	1.269	$281._8$	$282._2$	$-0._4$
74.6	25.4	20.3	44.1	1.314	$293._4$	$293._5$	$-0._1$
65.9	34.1	19.9	45.4	1.351	$304._9$	$303._5$	$+1._4$
64.5	35.5	19.9	45.7	1.360	$305._9$	$305._1$	$+0._8$
		18.0	45.4	1.361	$305._2$	$305._1$	$+0._1$
		20.0	45.2	1.360	$305._1$	$305._1$	$0._0$
48.4	51.6	20.4	46.1	1.420	$324._2$	$323._5$	$+0._7$
24.2	75.8	21.5	46.8	1.507	$350._4$	$351._4$	$-1._0$
		20.0	46.9	1.507	$350._5$	$351._4$	$-0._9$
19.6	80.4	19.0	46.9	1.519	$356._1$	$356._7$	$-0._6$
13.6	86.4	18.0	48.7	1.550	$363._1$	$363._5$	$-0._4$
		20.0	48.7	1.549	$363._3$	$363._5$	$-0._2$
0.0	100.0					379.3	

Table 3 gives the measured surface tensions and measured densities of solutions of nitroglycerine and nitrobenzene. It also compares values of the "parachor of the solution" derived from these with those deduced from the measured values for nitroglycerine (379.3) and nitrobenzene (264.3) on the assumption that the parachor of a solution has the average value of the parachors of its constituents, calculated according to their molecular proportions (2). The parachor is shown to be an additive property of the constituents.

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THE REDUCTION POTENTIAL OF DEVELOPERS AND ITS SIGNIFICANCE FOR THE DEVELOPMENT OF THE LATENT IMAGE

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Received January 16, 1934

I. INTRODUCTION

The development of the latent image on a photographic plate is a chemical reaction, which may be represented by the following equation:

$$\text{Ag Br} + \text{Red.} = \text{Ag} + \text{Ox.}$$

We can imagine this reaction occurring in a galvanic cell at the electrodes of which the following two electron reactions take place:

$$\text{AgBr} + \ominus = \text{Ag} + \text{Br}^-$$
$$\text{Red.} = \text{Ox.} + \ominus$$

The electromotive force of this cell is:

$$E = \epsilon_{\text{Ag}} - \epsilon_{\text{Redox}} \qquad (1)$$

The condition for reduction of the silver bromide is that the E.M.F. of this cell is positive. In this equation the silver potential is:

$$\epsilon_{\text{Ag}} = {}_{\text{Ag}}\epsilon_0 + \frac{RT}{F} \log L_{\text{AgBr}} - \frac{RT}{F} \log c_{\text{Br}^-} \qquad (2)$$

in which L_{AgBr} is the solubility product of silver bromide. At 18°C. (2)

$${}_{\text{Ag}}\epsilon_0 = 0.808 \text{ volt}$$

and[1]

$$L_{\text{AgBr}} = 3.6 \times 10^{-13}$$

so that at 18°C.

$$\epsilon_{\text{Ag}} = 0.086 - 0.058 \log c_{\text{Br}^-} \qquad (2a)$$

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[1] According to our own measurements. R. Cavanagh (J. Chem. Soc. 1927, 2207) found 3.13×10^{-13} at 16°C. Considering the large temperature coefficient this value agrees quite well with our measurements.

The concentration of the bromide in normal developers is about 0.01 molar.[2] Substituting this value in 2a, we obtain:

$$\epsilon_{Ag} = 0.202 \text{ volt at } 18°\text{C}.$$

The value of the redox potential will differ for the different developers. It is chiefly this value which determines the magnitude of E.

It may be expected that this last value will be of great importance for the rate of development. G. Bredig (1) was the first to draw attention to this point; he compiled a list of the reduction potentials of the various reducing agents which had been measured up to that time. His data relate however to rather arbitrary solutions and not to actual developer solutions. The great influence of the additions to these solutions, especially that of substances that alter the actual acidity, was not measured, so that no conclusions could be made about the relation between the reduction potential of a developer and its developing activity.

Other investigators as Sheppard and Mees (6), trying to measure the reduction potential of organic developers, found only inconstant and variable values. They consider, moreover, the reduction potential of little use in determining the reducing power, as other factors, such as the chemical resistance and the velocity of diffusion, interfere and will have a dominant influence on the velocity of reduction. Therefore these authors and also A. H. Nietz (4), instead of measuring the reduction potential along electrochemical lines, have sought a relation between the concentration of potassium bromide necessary to produce the same "density depression" at the same degree of development (γ) and the developing power of the developer. They introduce the term "relative reduction potential" and make the above-mentioned potassium bromide concentration proportional to this relative reduction potential. The real reduction potential cannot be calculated from their data, with the result that the relation between the real reduction potential and the developing power remains unknown.

II. THEORY OF THE LATENT IMAGE

Apart from the question about the importance of the reduction potential on the character of a developer, the knowledge of this potential is important for the theory of the latent image.

According to the germ theory of the latent image the first stage of the reduction process consists of a reaction of the reducing agent with the dissolved silver bromide, which results in the formation of a supersaturated solution of metallic silver. From this solution the silver may precipitate

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[2] The German Committee for Sensitometry has, at the 8th International Congress for Photography in Dresden, 1931, proposed as normal developer a metol-hydrochinon developer with 1 g. of potassium bromide per liter, that is, 0.0085 molar Br^-.

if silver nuclei, formed by the action of light, are present. If however no nuclei are present, the reaction stops when a certain degree of supersaturation has been reached and an equilibrium has been established, which means that the reduction reaction is counterbalanced by the opposing reaction between the oxidation product of the reducing agent and the metallic silver atoms in the solution.

The concentration of the metallic silver in this solution is determined by the reduction potential of the reducing agent.

In order to compute this concentration, c, we will introduce c_0—the concentration of the metallic silver in a solution, which is in equilibrium with large silver particles or with a silver plate—in equation 2:

$$\epsilon_{Ag} = \epsilon_0 + \frac{RT}{F} \ln c_{Ag^+} = \epsilon_0' + \frac{RT}{F} \ln \frac{c_{Ag^+}}{c_0}$$

Now, *if the concentration of the metallic silver is* c instead of c_0, then

$$\epsilon'_{Ag} = \epsilon_0' + \frac{RT}{F} \ln \frac{c_{Ag^+}}{c} = \epsilon_{Ag} - \frac{RT}{F} \ln \frac{c}{c_0}$$

For equilibrium

$$\epsilon'_{Ag} = \epsilon_{Redox}$$

Thus:

$$\epsilon_{Ag} - \epsilon_{Redox} = \frac{RT}{F} \ln \frac{c}{c_0} \qquad (3)$$

Introducing the value of ϵ_{Ag} at 18°C. in equation 2a, we obtain:

$$0.058 \log \frac{c}{c_0} = 0.086 - 0.058 \log c_{Br^-} - \epsilon_{Redox} \qquad (3a)$$

In measuring the reduction potential we are now able to calculate $\frac{c}{c_0}$ and $\frac{c-c_0}{c_0}$, that is, the degree of supersaturation of the supersaturated silver solution.

M. Volmer (8), in a somewhat different way, viz., based on Sheppard's measurements of the equilibrium between silver, silver bromide and a solution of ferrous-ferric oxalate, made an estimation of the supersaturation in a normal ferrous oxalate developer, which is in contact with silver bromide. He arrived at the proportion $c:c_0 = 2000$, which he thought improbably high and he rejected the silver germ theory of the latent image on this ground. In a later publication (9) he thinks this proportion quite possible, however.

III. SOLUBILITY AND SIZE OF THE SILVER PARTICLES

In equation 3, c_0 represents the concentration of the metallic silver in equilibrium with large silver particles or with a silver plate. In the latent image, however, we are dealing with extremely small silver particles, which have a much greater solubility than compact silver.

The connection between the solubility and the dimensions of a particle is given by the equation of Thomson-Ostwald[3] (7):

$$RT \ln \frac{c}{c_0} = 2\sigma \frac{M}{d} \cdot \frac{1}{r} \tag{4}$$

in which c_0 is the solubility of large particles, c is the solubility of globular solid particles with the radius r, $\frac{M}{d}$ = molecular volume of the solid substance, and σ is the surface tension at the surface solid–solution.

For silver at 18°C. $\frac{M}{d} = \frac{108}{10.5} = 10.3$, $T = 291$, $R = 8.32 \times 10^7$. σ is unknown. We will take for σ the same value as for the surface tension of liquid silver against air at 950°C., namely 750 (3), although we have no reason to suppose that this is the right value. We find then:

$$\log \frac{c}{c_0} = \frac{2\sigma}{2.3RT} \cdot \frac{M}{d} \cdot \frac{1}{r} = 2.8 \times 10^{-7} \cdot \frac{1}{r} \tag{5}$$

It is clear that for all values of r greater than 10^{-5}, $\log \frac{c}{c_0}$ is very small and c practically equal to c_0.

For a particle of $10\mu\mu$ ($r = 5 \times 10^{-7}$ cm.) $\log \frac{c}{c_0} = 0.56$ and $\frac{c}{c_0} = 3.6$; for a particle of $2\mu\mu$, however, $\frac{c}{c_0} = 900$.

This shows that the value of c increases very rapidly, as the diameter of the particle decreases. A silver globule of $2\mu\mu$ diameter is still relatively large; it contains about five hundred atoms. The germs of the latent image are far smaller. According to the researches of Reinders and Hamburger (5), confirmed by quite other experiments of Chr. Winther (10), they will be aggregates of about four atoms. Equation 5 would give for such an aggregate a solubility nearly 10^{10} times greater than c_0.

Equation 4, however, is not applicable to such small particles, as the surface tension has lost its significance. The factor σ will just as well become a function of r and will diminish with r. Decreasing of r will therefore not increase the solubility as much as indicated by equation 4.

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[3] Ostwald gave this formula with the coefficient 3 instead of 2. H. Freundlich (Kapillarchemie, 4th edition, Vol. I, p. 218) has demonstrated that this factor must be 2.

Qualitatively, however, we can say that with these small aggregates the solubility will decrease by steps as the aggregate increases with one or two atoms; the curve will have a shape as sketched in figure 1.

A solution of the concentration *c* will be just saturated with respect to particles of the size *a*. With respect to larger particles it will be supersaturated; hence these larger particles will act as germ and cause crystallization. With respect to smaller particles, the solution is unsaturated. These particles cannot act as germ; on the contrary they will dissolve.

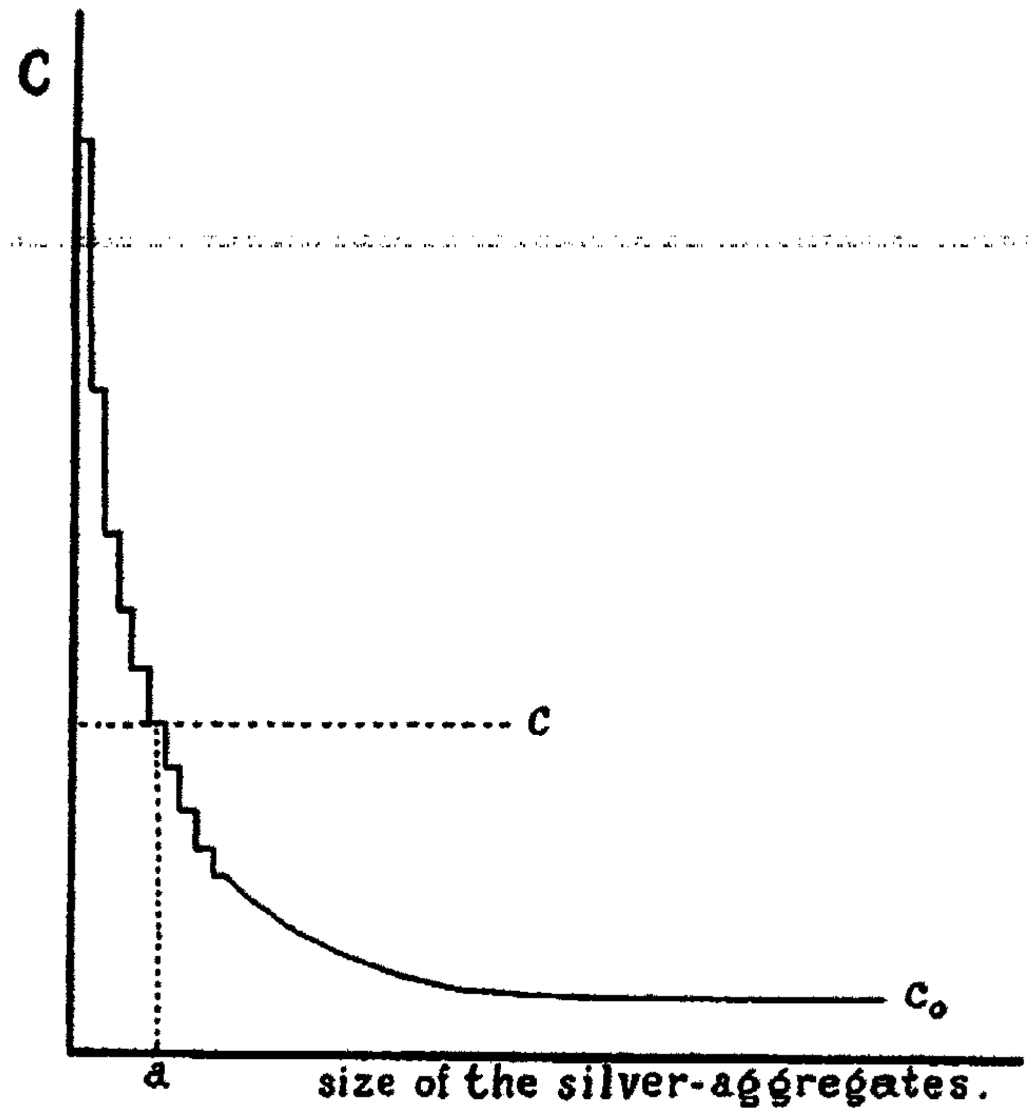

FIG. 1. SOLUBILITY OF SILVER PARTICLES AS A FUNCTION OF THEIR SIZE

Therefore, if in the latent image the germs have the size *a*, the developer must have a redox potential low enough to produce with the silver bromide a silver solution of a higher concentration than *c*, for it to be able to develop this latent image.

This redox potential must be lower than the redox potential that corresponds to the solubility of large silver particles.[4] By measuring the differ-

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[4] We suppose the possibility of the spontaneous formation of nuclei in this case as excluded. For this spontaneous formation it would be necessary that the gap between single atoms and particles of the size *a* is bridged over, that the aggregation of these particles is established in some way or other. Without forming an exact idea about the mechanism of this process, it is obvious that in general it will be

ence $E = \epsilon_{Ag} - \epsilon_{Redox}$ that is just necessary to develop the latent image, we will be able to calculate the supersaturation, c, that corresponds to the solubility of the particles of the latent image.

IV. EXPERIMENTAL PROOF OF THE THEORY

To prove this theory experimentally one must have a set of solutions with ascending redox potential, each of which is quite constant and exactly measurable.

Such solutions can be made by adding various amounts of sodium citrate or sodium malonate to a mixed solution of a ferrous and a ferric salt. If the concentration of the iron salts is sufficiently high and the proportion ferrous:ferric is nearly 1:1, then the solution has a great buffering capacity The potential is very constant, and remains constant, also when the solution comes in contact with the air or after it has reduced a considerable part of the silver bromide in a plate to silver.

TABLE 1

Measurement of redox potentials

Always 20 cc. of a solution with 0.125 mole $FeSO_4$ and 0.125 mole $Fe(SO_4)_{1.5}$ per liter

ABOVE SOLUTION + x CC. OF 1 MOLAR SODIUM CITRATE		ABOVE SOLUTION + x CC. OF 1 MOLAR SODIUM MALONATE	
x	Redox potential	x	Redox potential
cc.		cc.	
0	+0.645	0	+0.645
1	0.625	1	0.620
2	0.600	2	0.596
3	0.545	3	0.552
3.5	0.480	4	0.477
4	0.380	5	0.380
4.5	0.265	6	0.262
5	0.205	7	0.175
6	0.150	8	0.122
7	0.110	9	0.092
8	0.085	10	0.071
9	0.070	12	0.050
10	0.060	16	0.021

We made a solution of 0.125 mole $FeSO_4 \cdot (NH_4)_2SO_4 7aq$ and 0.125 mole $FeNH_4(SO_4)_2 \cdot 12aq$ per liter and added to 20 cc. of this solution increasing quantities of a 1 molar solution of sodium citrate or sodium malonate.

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performed more easily, the narrower this gap is, that is, the smaller the particles a are. Spontaneous formation of nuclei, manifested by fogging of the plate, will thus appear more easily, the higher the supersaturation, that is, the lower the redox potential of the developer.

The redox potential of these solutions was measured with a platinum electrode at 20°C. and with a calomel electrode as second electrode. The values obtained are inserted in table 1 and in figure 2.

The potentials are very constant. Addition of 1 or 2 cc. of 0.1 normal sulfuric acid has little influence. The solutions are quite clear yellowish green and remain clear after standing for several days.

By increasing the proportion $Fe^{++}:Fe^{+++}$, the steep fall of the potential, which in the solutions of table 1 may be observed on addition of about 4 cc.

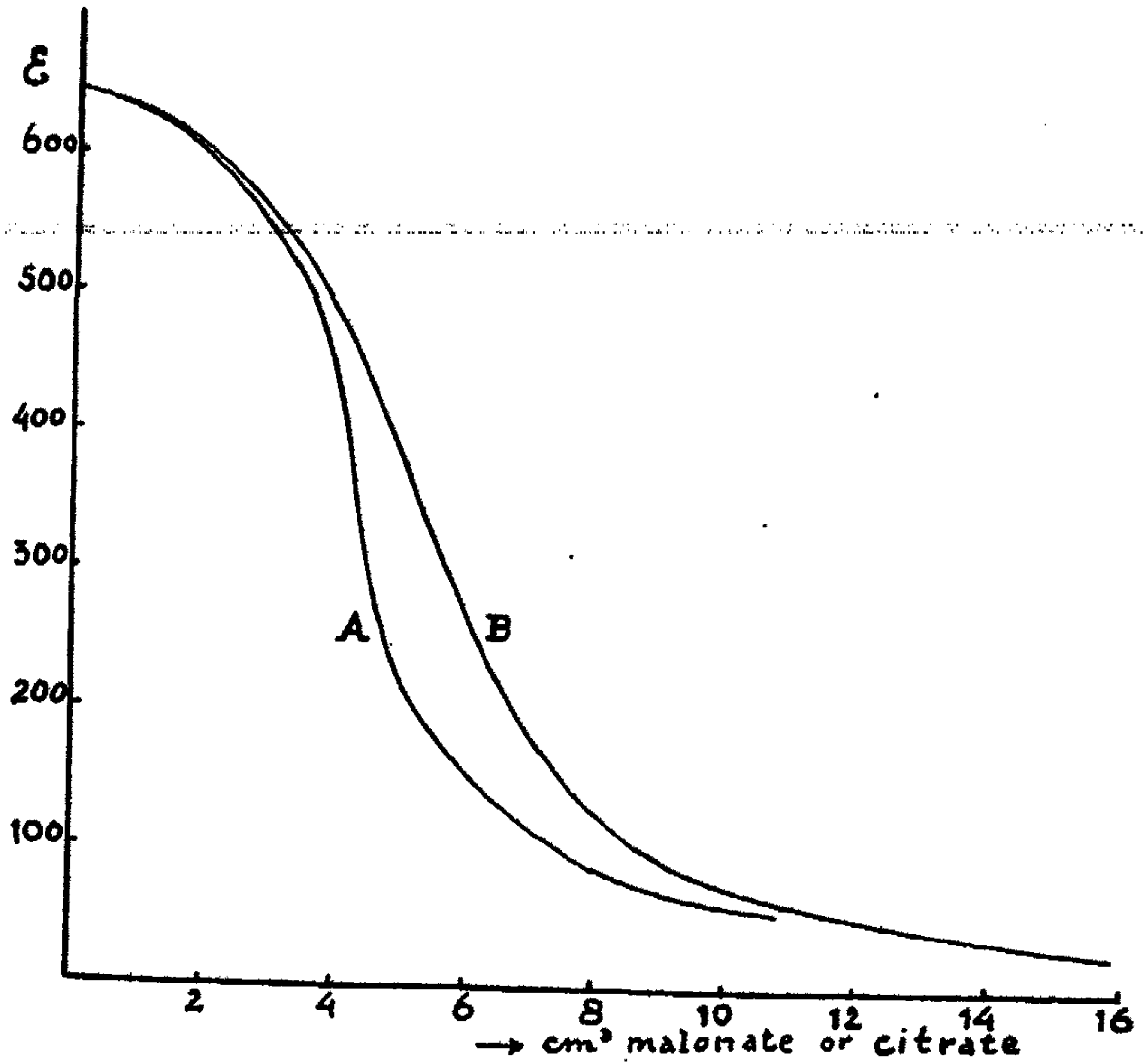

FIG. 2. REDOX POTENTIAL OF FERROUS-FERRIC SULFATE ON ADDITION OF SODIUM CITRATE OR SODIUM MALONATE

of citrate, sets in sooner, while also somewhat lower potentials may be obtained.

By selecting a proper proportion of the different ingredients, it is thus easily possible to prepare solutions in which the redox potential has any value desired between 300 and 0 millivolts.

V. VERIFICATION OF EQUATION 1

To verify now equation 1 and the conclusions that may be drawn from this equation, firstly it ought to be proved, that the reduction of silver

TABLE 2

Density of equally exposed strips of an Agfa Isochrom film, partly predeveloped to D=0.82 in metol-borax and then during twenty hours immersed in ferrous-ferric solutions with the indicated redox potential

NO. OF STRIP	DENSITY OF THE PARTLY DEVELOPED HALF	DENSITY OF THE NOT PREDEVELOPED HALF	REDOX POTENTIAL	$E = \epsilon_{Ag} - \epsilon_{Redox}$
			mv.	mv.
1	0.16	0.10	303	−101
2	0.40	0.10	241	−39
3	0.82	0.10	202	0
4	0.82	0.10	200	+2
5	1.48	0.10	156	+46
6	2.53	0.15	113	+89
7	3.00	2.90	62	+140
8	3.00	3.00	22	+180
9	0.82	0.10		

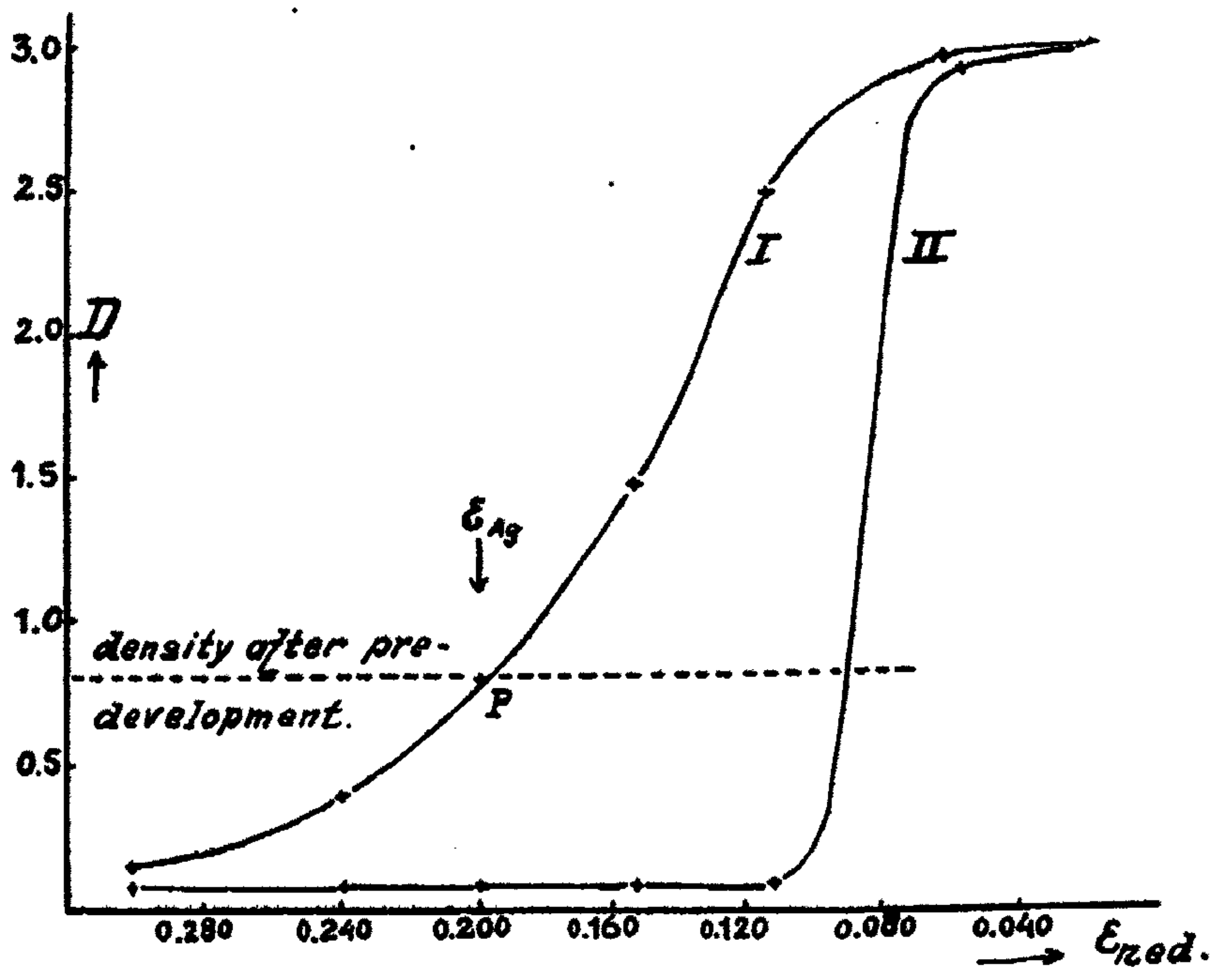

FIG. 3. DENSITY OF EQUALLY EXPOSED STRIPS OF AN AGFA ISOCHROM FILM AFTER IMMERSION IN FERROUS-FERRIC SOLUTIONS WITH THE INDICATED REDOX POTENTIAL

I, after exposure predeveloped in metol-borax; II, as I, but not predeveloped.

bromide proceeds in a developer solution with a lower redox potential than the silver potential and that resolution of reduced silver takes place in a solution with higher redox potential than the silver potential. For this purpose an Agfa Isochrom film was so long exposed, that, developed normally with a normal developer, it would obtain a density of about 3 (about 20 M.C.S.). The film was then half dipped in a metol-borax developer, wherein it obtained in 1 minute a density of 0.82.

The whole film was now thoroughly washed and cut in nine strips 1.3 × 9 cm., so that one half of each strip was partly developed to a density 0.82 and the other half was well exposed, but not developed. Eight of these strips were placed in tubes, nearly totally filled with 25 cc. of the above mentioned ferrous–ferric citrate solutions, which by addition of potassium bromide were made exactly 0.01 molar with respect to potassium bromide. The tubes were closed with a rubber stopper and during 20 hours kept at 18 to 20°C. The ninth strip, used for control, remained in pure water. After expiration of this time the strips were thoroughly washed and fixed, washed and dried. The density was then measured with the Goldberg densograph. The redox potential of the ferrous–ferric solutions was again measured as the strips were taken out. We found the results given in table 2.

In figure 3 the densities are represented in graph form as a function of the redox potential. The density 0.82, obtained by the predevelopment, is indicated by the dotted line, the final densities of the predeveloped parts by curve I, and those of the not predeveloped parts by curve II.

VI. CONCLUSIONS AS TO THE SOLUBILITY OF THE SILVER PARTICLES AND THE DEVELOPMENT OF THE LATENT IMAGE

From this experiment we may draw the following conclusions:

(1) The density arrived at by the predevelopment is intensified by a subsequent development in solutions with a lower redox potential than 200 millivolts and decreased by the subsequent action of a solution with a redox potential higher than 200 millivolts. The silver and silver bromide in the plates are thus in equilibrium with solutions containing 0.01 mole of potassium bromide per liter and having a redox potential = 200 millivolts. That, as we have seen on page 784, is exactly the potential of Ag/AgBr, 0.01 molar KBr in case of large silver particles. *This proves that the solubility of the silver particles in the developed plates is equal to the normal solubility of silver.*

Close to the equilibrium point *P*, curve I is nearly a straight line. Thus, the increase of density, which means the velocity of development, is proportional to the potential difference $E = \epsilon_{Ag} - \epsilon_{Redox}$, while also the decrease of density, that is the velocity of dissolution of silver, is proportional to the potential difference $\epsilon_{Redox} - \epsilon_{Ag}$.

(2) Curve II, giving the density by developing the latent image, is quite different. While the predeveloped part of the film is at once further developed as the redox potential sinks under the normal silver potential, the latent image shows no developing before the redox potential has reached the value 120 millivolts, that is, about 80 millivolts under the normal silver potential. As the difference $\epsilon_{Ag} - \epsilon_{Redox}$ increases, soon a normal developing is attained, giving the same density as the predeveloped films. Mr. M. C. F. Beukers has, on my request, repeated this experiment with other plates and other reducing solutions and obtained always similar results: *The development of the latent image does not begin before the redox potential of the developer has sunk 70 to 90 millivolts under the normal silver potential.*

VII. RESULTS OF SHEPPARD AND MEES

This result does not agree with the results of somewhat similar experiments described by Sheppard and Mees in their investigations on the theory of development. They determined the equilibrium

$$Ag^+ + Fe(C_2O_4)_2^{--} \rightleftarrows Ag(\text{metal}) + Fe(C_2O_4)_2^-$$

and found that the compositions of the mixtures of ferrous oxalate, ferric oxalate and potassium bromide, in which a negative of known density did not bleach further and of those in which the latent image of an exposed plate did not develop further, were practically equal. This would mean that curves I and II in figure 3 should coincide. Our experiments prove that this is not the case.

We cannot explain the discrepancy. Possibly Sheppard and Mees have used an extremely long exposure, so that the plate was partly blackened by the light. We must however remark that their experiments, in which they used 25 cc. of solution, containing at the utmost 0.000092 gram-mole of ferrous salt (equivalent to 0.5 cc. of oxygen), and mixed with a fifty times greater amount of ferric salt, cannot be very accurate. A slight oxidation of the ferrous salt will have a great influence on the redox potential.

VIII. SILVER PARTICLES IN THE LATENT IMAGE

From the conclusions mentioned in section VI it follows that the silver particles in the latent image have a much greater solubility than compact silver has. With the value $\epsilon_{Ag} - \epsilon_{Red.} = 0.080$, we can calculate the proportion $c:c_0$

$$0.058 \log \frac{c}{c_0} = 0.080 \quad \text{or} \quad c:c_0 = 25$$

The solubility of the silver nuclei in the latent image is, according to this formula, about twenty-five times as great as that of compact silver.

Equation 5 gives for the dimensions of these nuclei:

$$r = \frac{2.8 \times 10^{-7}}{\log c:c_0} = 2 \times 10^{-7} \text{ cm.}$$

Particles of this dimension will be aggregates of some hundreds of atoms. This is not in agreement with the results of Reinders and Hamburger which made it probable that these germs are aggregates of a very few atoms, e.g., 4 or 5. Now we have already demonstrated that equation 5 cannot be valid for such extremely small particles, as for those particles the value of σ will be only a fraction of the surface tension of compact silver. If we let σ equal not 750, but a value five times smaller, for instance, then we find $r = 3.6 \times 10^{-8}$ cm., a value that does agree very well with the results of Reinders and Hamburger.

TABLE 3

Redox potential of the solutions relating figures 4 and 5

NO. OF STRIP	REDOX POTENTIAL	$\epsilon_{Ag} - \epsilon_{Redox}$
	mv.	*mv.*
1	171	31
2	130	72
3	105	97
4	75	131

IX. DISAPPEARANCE OF THE LATENT IMAGE

Another conclusion may be drawn from the discussion in section III. The silver particles of the latent image, having a solubility that corresponds with a redox potential of 120 millivolts in a 0.01 molar potassium bromide solution saturated with silver bromide, are not in equilibrium with solutions with higher redox potential. In a solution with a redox potential between 200 and 120 millivolts—in which the partly developed silver bromide grains are further developed—these germs will dissolve. *The latent image will in these solutions diminish or disappear.*

This conclusion was proved in the following experiment: Five strips of the same film that had been used for the experiments in section V (Agfa Isochrom), numbered 1 to 5, were all exposed in the same way behind a Goldberg density wedge. Four of them were immersed in different ferrous-ferric citrate solutions, all containing 0.01 mole of potassium bromide per liter, and having a redox potential varying from 171 to 75 millivolts, as indicated in table 3. They remained in these solutions (in closed tubes) for 18 hours at 18°C. The fifth strip, used for control, remained during

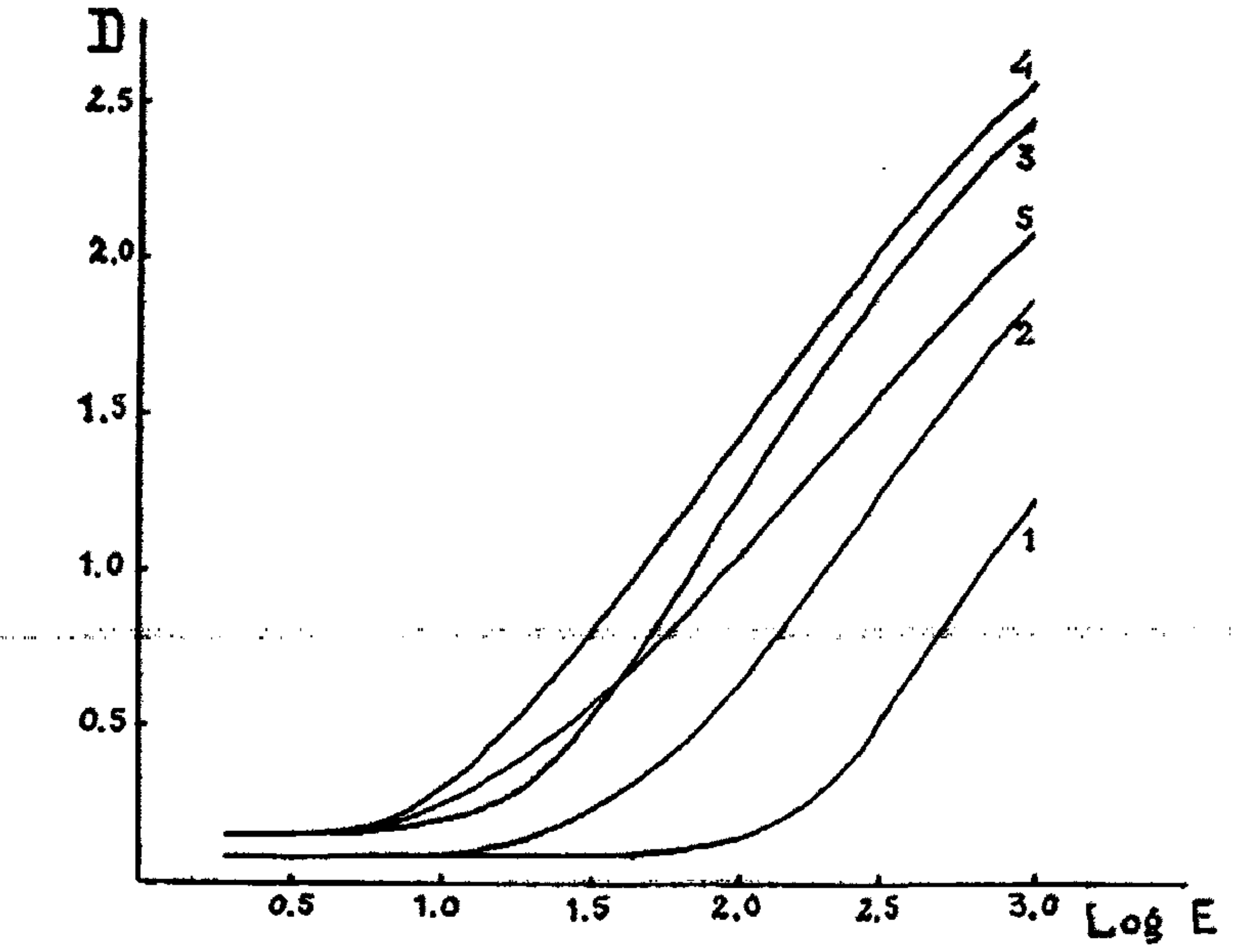

FIG. 4. CHARACTERISTIC CURVES OF AGFA ISOCHROM STRIPS, DEVELOPED IN A STANDARD METOL-BORAX DEVELOPER AFTER PRETREATMENT WITH FERROUS-FERRIC CITRATE SOLUTIONS OF VARIOUS REDOX POTENTIAL

ϵ_{Redox} for 1 = 170, for 2 = 130, for 3 = 105 and for 4 = 75 mv. No. 5 untreated.

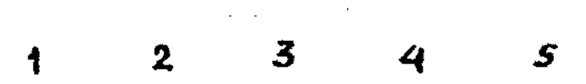

FIG. 5. STRIPS OF AN AGFA ISOCHROM PLATE, AFTER EXPOSURE BEHIND A DENSITY WEDGE, TREATED WITH FERROUS-FERRIC SOLUTIONS OF VARIOUS REDOX POTENTIAL AND THEN DEVELOPED IN A STANDARD METOL-BORAX DEVELOPER

this time in pure water. On expiration of this period, Nos. 3 and 4 were faintly developed in the more highly exposed parts; Nos. 1 and 2 were apparently unaltered. All the strips were washed for an hour in running water and then developed for 6 minutes in a standard metol-borax developer,[5] fixed, washed and dried. Figure 4 gives the resulting characteristic curves. Figure 5 shows the developed strips of a duplicate experiment with Afga Isochrom plates.

The characteristic curves for solutions 1 and 2 lay beneath, those for solutions 3 and 4 somewhat above the control curve 5. In solutions 3 and 4 the redox potential is so low that $\epsilon_{Ag} - \epsilon_{Red.}$ surpasses the limit of 80 millivolts, mentioned in section VI. In these solutions the latent image is slightly developed and made visible by the subsequent development in the metol–borax solution.

In solutions 1 and 2, however, the latent image is partly dissolved, although the redox potential is below the normal silver potential in these solutions. This result is in perfect agreement with our predictions. It proves once more the far greater solubility of the silver germs of the latent image.

Comparing the form of the characteristic curve of the normally developed strip 5 with those of the strips that were pretreated with the iron citrate solutions, it is surprising to observe that the latter are steeper. Curve 3 and 5 even intersect, so that the weakly exposed parts in 3 are less developed than in 5, whereas the strongly exposed parts are more developed. This is what could be expected. Indeed, it is probable that the latent image in the weakly exposed parts will, on the average, be composed of smaller silver germs than those in the strongly exposed parts, so that they have a greater solubility. In a solution with a reduction potential about 90 millivolts lower than the normal silver potential in that solution, they will dissolve, whereas the larger silver aggregates will act as germ and will be developed.

This is an indication that the limit of 70 to 90 millivolts for the difference $\epsilon_{Ag} - \epsilon_{Red.}$, which must be surpassed to make the latent image developable, is not a constant value, but will depend on the exposure that has been given.

We will make further researches in regard to this point.

X. SUMMARY

1. The latent image of a normally exposed photographic plate is not developed unless the developer has a reduction potential of at least 70 millivolts below the silver potential in the solution.

2. From this fact it follows that the silver germs in the latent image have a solubility about twenty-five times the normal solubility of large silver particles.

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[5] This solution contained in a liter: 0.05 mole metol (8.6 g.), 0.05 mole borax (19 g.), 0.05 mole sodium carbonate (5.3 g.), 0.3 mole $Na_2SO_3 \cdot 7H_2O$ (75 g.), and 0.5 g. potassium bromide. See Reinders, W., and Beukers, M. C. F.: Ber. 8th Intern. Kongr. Phot. Dresden, p. 171 (1931).

3. By addition of sodium citrate or sodium malonate to a mixture of ferrous and ferric salt, solutions with great buffer capacity may be prepared, having a reduction potential between 300 and 0 millivolts.

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THE COLOR AND CRYSTAL STRUCTURE OF PRECIPITATED CADMIUM SULFIDE

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Received December 15, 1933

Cadmium sulfide may be either yellow or red, depending on the conditions of formation. Earlier investigators (3) attributed this difference in color either to the presence of impurities or to the existence of yellow and red allotropic modifications of the compound. The possibility that the difference in color was due to allotropy was questioned by Allen and Crenshaw (1), who prepared crystals of the compound by a variety of methods and found them to be identical in structure with the mineral greenockite, irrespective of the method of formation and the color. It was concluded therefore that the differences in color were due to differences in the physical character, such as particle size and the nature of the surface of the particles, rather than to allotropy. The yellow form is usually obtained by precipitation from alkaline or cold solutions, and the orange or red from acid or hot solutions. Heating the yellow material gives an orange to red colored product, the change being more or less reversible on cooling (6).

In the absence of x-ray diffraction methods of examination, Allen and Crenshaw (1) were unable to determine the structure of the extremely minute crystals of the freshly precipitated salt and were forced to grow them to a size that could be observed optically, either by heating the dry powder or by digesting the mass under pressure at high temperatures. This always yielded hexagonal crystals like greenockite, but Böhm and Niclassen (2) showed by x-ray diffraction methods that the yellow precipitate thrown down from cadmium sulfate solution was cubic, being similar to the cubic zinc blende. This was confirmed by Ulrich and Zachariasen (5), who showed that cubic or β cadmium sulfide ($a_0 = 5.820$ Å.) was precipitated from a saturated cadmium sulfate solution by hydrogen sulfide and dried at 70°C. On heating this yellow cubic sulfide to 700–800°C. in the presence of sulfur vapor, hexagonal or α cadmium sulfide resulted. There is therefore no doubt of the existence of two polymorphic forms of the sulfide, but since both the cubic and the hexagonal forms may be yellow, it is obvious that the color differences are not due to polymorphism. Within the current year Müller and Löffler (4) precipitated cadmium sulfate solutions containing varying amounts of sulfuric acid with hydrogen sulfide, and obtained precipitates which varied in color from yellow to red, the samples being more red the higher the concentration of acid. Since all of these preparations gave a cubic x-ray diffraction pattern, the differences in color were attributed to variation in particle size. It would appear from the x-ray studies of the gel that precipitated cadmium sulfide is always cubic, the hexagonal form resulting only after subjecting the gelatinous mass to high temperatures. Such is not the case, as the following experiments show.

TABLE 1

Color and crystalline form of precipitated cadmium sulfide

CADMIUM SALT USED	WITHOUT THE ADDITION OF ACID				IN THE PRESENCE OF ADDED ACID			
	At 30°C.		At 100°C.		At 30°C.		At 100°C.	
0.1 *N*	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form
Sulfate..........	Yellow	Hexagonal*	Yellow	Cubic	Yellow	Cubic†	Red	Cubic
Nitrate..........	Yellow	Hexagonal	Yellow	Hexagonal*	Yellow	Cubic†	Red	Cubic
Chloride..........	Yellow	Hexagonal*	Yellow	Hexagonal	Yellow	Hexagonal	Red	Hexagonal
Bromide..........	Yellow	Hexagonal*	Yellow	Hexagonal	Orange	Hexagonal	Red	Hexagonal
Iodide..........	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal

* Trace of cubic β cadmium sulfide.

† Trace of hexagonal α cadmium sulfide.

TABLE 2

X-ray diffraction data

α CADMIUM SULFIDE PRECIPITATED AT 100°C. FROM $CdCl_2$, ACID		β CADMIUM SULFIDE PRECIPITATED AT 100°C. FROM $CdSO_4$, ACID	
d_{hkl}	I	d_{hkl}	I
3.55	9	3.36	10
3.34	8	2.90	3
3.14	10	2.06	10
2.43	4	1.756	9
2.06	10	1.683	1
1.888	8	1.456	1
1.750	9	1.335	2
1.668	1	1.302	1
1.567	1	1.189	3
1.390	2	1.121	3
1.320	1	1.026	2
1.248	2	0.982	2
1.187	1		
1.150	1		
1.125	1		
1.066	1		
0.982	1		

EXPERIMENTAL

Hydrogen sulfide was passed into approximately 0.1 *N* solutions of cadmium sulfate, nitrate, chloride, bromide, and iodide at both 30°C. and 100°C. In a second series of experiments the solutions were made acid by the addition of 1 cc. of the corresponding "concentrated" acid to 50-cc. portions of the various cadmium salt solutions. The twenty samples were washed and dried at room temperature. Some of the samples from the bromide and iodide solutions formed very stable sols, and were precipitated by the addition of ether or alcohol. The various samples were examined by the x-ray diffraction method, using the General Electric diffraction apparatus. The observations of crystal form and color are listed in table 1. Typical patterns are shown in chart form in figure 1.

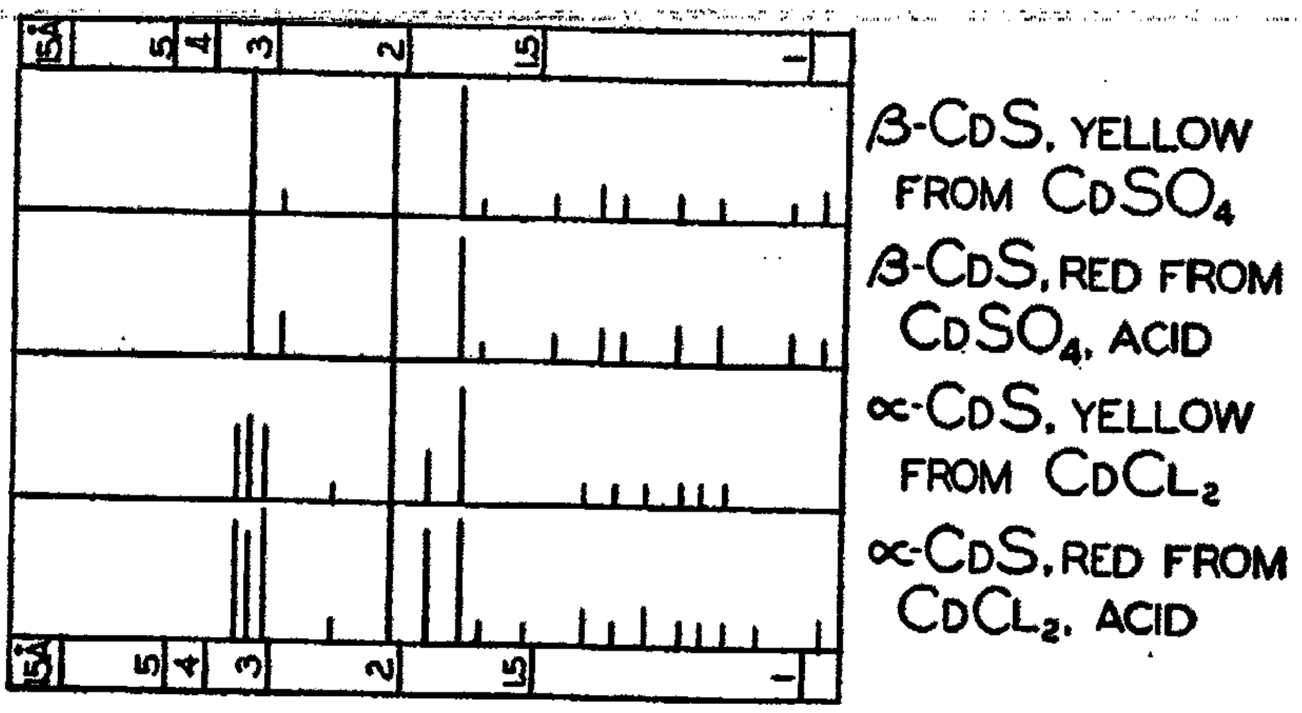

FIG. 1. α AND β CADMIUM SULFIDE PRECIPITATED AT 100°C.

Typical diffraction data are recorded in table 2; the values for the lattice constants of various samples agree within experimental error with the values of Ulrich and Zachariasen (5).

CONCLUSIONS

Inspection of the results in table 1 and figure 1 shows that either the cubic or hexagonal modifications of cadmium sulfide may be yellow or red (or orange), depending on the conditions of formation and treatment. All samples appear more or less orange upon grinding the dry aggregates to a powder. The cubic form is usually obtained from the sulfate or nitrate solution, especially from hot or acid solutions. The hexagonal modification is usually obtained from the chloride, bromide, or iodide solutions. Small amounts of the cubic form sometimes occur in essentially hexagonal precipitates; this is probably more or less accidental, depending upon slight variations in the conditions of precipitation. The difference in color must be attributed to difference in the physical character of the precipitate, such as particle size, the nature of the surface of the particles, and the state of aggregration. Difference in particle size alone will not suffice to explain all the known facts, since large crystals of greenockite are yellow, although red (or orange) particles are usually larger and more granular than the yellow ones. The view that color differences are essentially due to differences in physical character of the samples is in agreement with the observation that the red particles obtained from hot acid solutions possess less adsorptive capacity than the yellow particles formed in the cold (7).

SUMMARY

The following is a brief summary of the results of this investigation:

~~1. Either cubic β cadmium sulfide or hexagonal α cadmium sulfide may~~ be yellow or red, depending upon the physical character of the precipitate.

2. The β cadmium sulfide tends to be precipitated from cadmium sulfate solutions, and under some conditions from the nitrate solutions, especially if the latter are hot and distinctly acid in reaction.

3. The α cadmium sulfide tends to be precipitated from the chloride, bromide, and iodide solutions, but these precipitates may also contain some of the β modification.

4. The lattice constants found for the two modifications of cadmium sulfide agree within experimental error with those of Ulrich and Zachariasen.

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LIQUID AMMONIA AS A SOLVENT. II

VAPOR PRESSURES OF SOLUTIONS AT 25°C.[1]

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Received September 26, 1933

These investigations were made in order to establish a significant scale of relative acidities, basicities, and salt-like properties in liquid ammonia and water. The present part deals with the vapor pressures of the more concentrated solutions of ammonium salts in liquid ammonia. These data may help to interpret the complex ammonia system of electrolytes.

EXPERIMENTAL

Manometer

The vapor pressures were measured directly on a manometer capable of reading fifteen atmospheres pressure (figure 1). The millimeter scale for this manometer was calibrated with a U. S. Bureau of Standards steel tape. The readings were corrected for temperature and gravity so that the vapor pressures are expressed in centimeters of mercury at 0°C. and a gravitational acceleration of 980.665 cm. per $sec.^2$ It was found that the correction for the compressibility of water only amounted to 0.001 per cent at 750 cm. pressure; it was therefore neglected. The manometer was filled with boiled water, all air bubbles being carefully removed. Columns A and F were carefully dried after the manometer was filled. The pressure of the water columns, calculated to standard conditions, was subtracted from the mercury reading and the barometric pressure added. As a final check on this method of measurement the vapor pressure of pure ammonia was measured. We obtained a value of 750.8 cm. as compared to 752.05 reported by Cragoe (1). When the initial pressure was not more than three atmospheres (concentrated solutions), a simple manometer was used.

Temperature

A double-walled copper container of 1-gallon capacity was immersed in a 75-gallon water thermostat. The Dewar containing the cell was placed

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[1] This paper is a part of a thesis presented by W. E. Larsen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Purdue University.

inside this adjustable container. This triplex system made it convenient to surround the cell with a carbon dioxide–ether bath for chilling and also to minimize temperature changes. The room was kept at a temperature such that the vapor pressure of ammonia was several centimeters above the vapor pressure of the solution, so that ammonia would not condense in the exposed tubes. The thermostat was kept at 25°C. ± 0.025°C., so the Beckmann (U. S. Bureau of Standards calibration) thermometer in the Dewar was constant to ±0.001°C. over a long period of time.

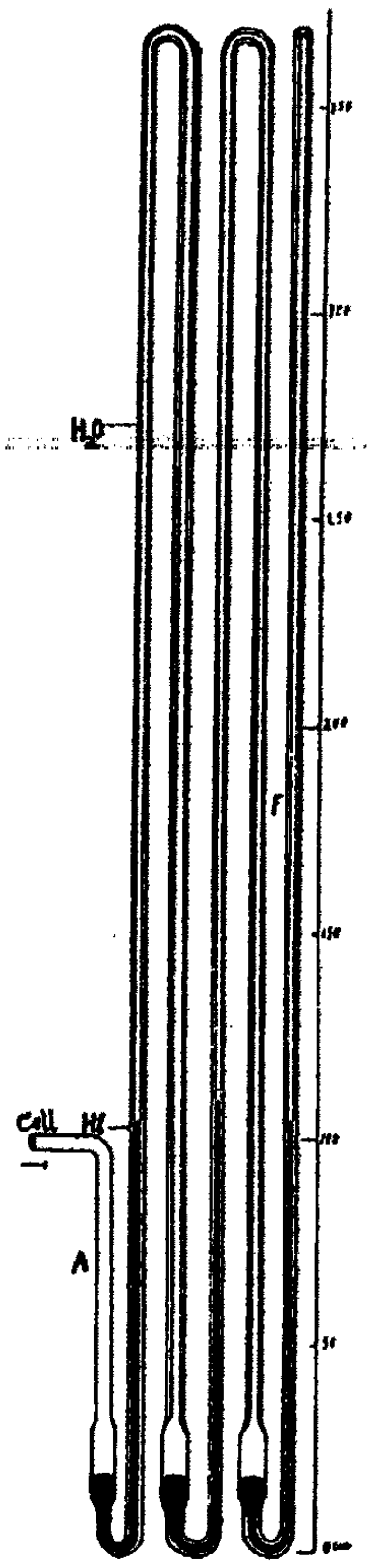


FIG. 1. MANOMETER

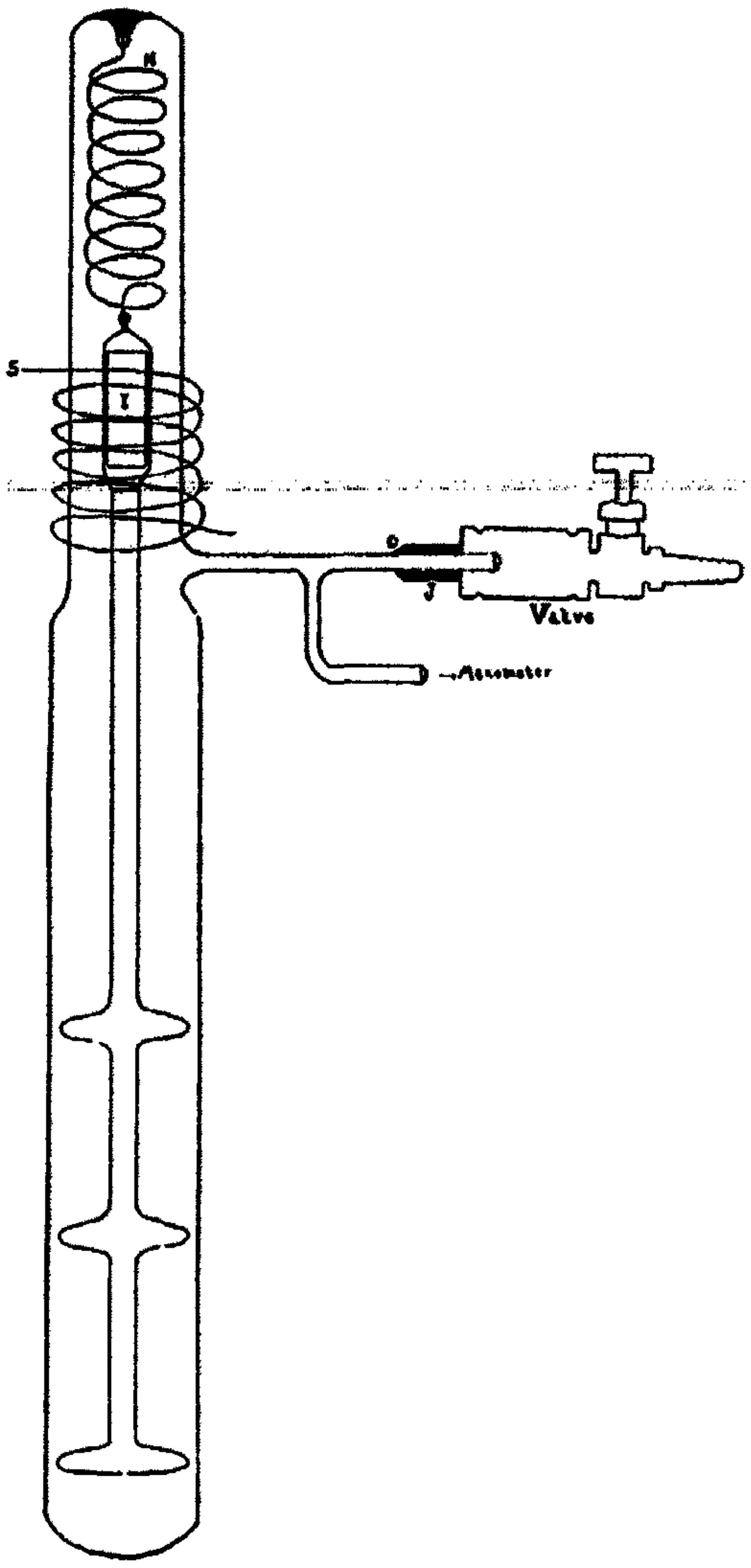


FIG. 2. THE CELL

Cell

Figure 2 shows the electrically stirred cell used for the solutions. An intermittent current passed through S. V is an iron needle valve used in valving the ammonia when it was desired to change the concentration. The cell had a volume of 100 ml. The vapor space over the solution and in the tube leading to the manometer was measured gravimetrically. This space is reduced to a minimum.

Measurements

Reagent grade salts were recrystallized from water three times and dried for several hours at 110°C. They were placed in the cell and an excess of ammonia condensed into it. The cell was then sealed in place and the system evacuated while chilled. The cell was then warmed with the valve closed until the vapor pressure was several atmospheres. By repeated warming, chilling, and pumping out, the cell and manometer were freed from air. In order to keep the ratio of ammonia in the solution to ammonia in the vapor phase high, it was necessary to use larger amounts of ammonia for the dilute solutions. The series varied from 13 g. of salt and 3 g. of ammonia to 0.4 g. of salt and 20 g. of ammonia. From three to

TABLE 1

Vapor pressures of ammonium nitrate in liquid ammonia at 25°C.

SERIES	$\frac{\text{MOLES NH}_3}{\text{MOLE NH}_4\text{NO}_3}$	P	SERIES	$\frac{\text{MOLES NH}_3}{\text{MOLE NH}_4\text{NO}_3}$	P
		cm. Hg			*cm.* Hg
A	0.744	86.3	C	8.01	613.0
B	0.808	86.3	D	9.10	638.1
A	1.22	88.0	E	11.4	672.6
C	1.30	97.0	F	12.2	682.7
C	1.56	123.0	E	15.6	699.2
B	1.76	143.4	E	21.7	716.6
A	1.85	152.9	F	32.6	727.9
D	1.93	163.5	E	47.3	735.5
D	2.20	192.6	E	51.8	736.6
C	2.58	235.8	G	60.0	738.7
D	2.84	266.7	G	69.7	740.4
C	3.09	291.4	G	80.6	741.7
C	3.45	331.1	G	91.4	742.6
C	4.01	385.9	G	111	743.7
D	4.55	438.6	F	126	744.4
D	5.23	489.1	F	135	744.8
D	6.30	551.1	F	140	745.0
C	7.05	580.7			

six hours were allowed for equilibrium to be established for the first reading and at least two hours for each subsequent reading. The manometer readings did not vary more than 1 mm. on standing an hour after equilibrium was reached.

The concentration was changed by allowing ammonia to escape through V and absorbing it in concentrated sulfuric acid. The concentration of the solution was calculated from the solvent and solute present in the cell at each reading, allowance being made for the ammonia in the vapor phase.

TABLE 2

Vapor pressures of ammonium iodide in liquid ammonia at 25°C.

SERIES	$\frac{\text{MOLES NH}_3}{\text{MOLE NH}_4\text{I}}$	P	SERIES	$\frac{\text{MOLES NH}_3}{\text{MOLE NH}_4\text{I}}$	P
		cm. Hg			*cm.* Hg
B	1.98	73.6	D	9.64	612.4
A	1.99	73.8	E	10.2	621.8
C	2.40	84.2	E	11.1	638.3
B	2.59	96.0	F	12.3	654.7
B	3.00	132.8	G	15.5	683.3
A	3.26	158.7	G	16.9	691.1
A	3.57	195.7	G	18.4	697.5
C	3.68	210.3	F	20.1	704.1
A	3.79	221.0	F	21.2	708.0
E	3.84	232.4	G	23.8	712.4
C	3.94	241.1	H	30.2	722.0
E	4.03	255.4	H	36.7	727.8
E	4.25	282.3	H	44.6	732.1
D	4.35	301.3	H	48.0	733.4
E	4.55	316.7	H	60.0	737.2
D	4.87	358.2	I	66.5	738.8
F	5.03	375.5	I	83.1	740.9
D	5.37	406.0	I	99.9	742.6
D	5.88	448.6	J	115	743.6
D	6.29	477.3	J	135	744.9
E	6.51	487.5	J	147	745.1
F	6.97	517.4	J	161	745.7
F	7.74	553.0	J	177	746.0
D	8.48	580.7	J	200	747.1

The weight of salt was determined at the end of a run by weighing the cell and salt and then weighing the cell after the salt had been dissolved out.

RESULTS AND CALCULATIONS

The values given in tables 1, 2, 3, and 4 are the values obtained from several sets of independent measurements. These values of the vapor pressures are plotted in figures 3 and 4, where the concentration is ex-

TABLE 3

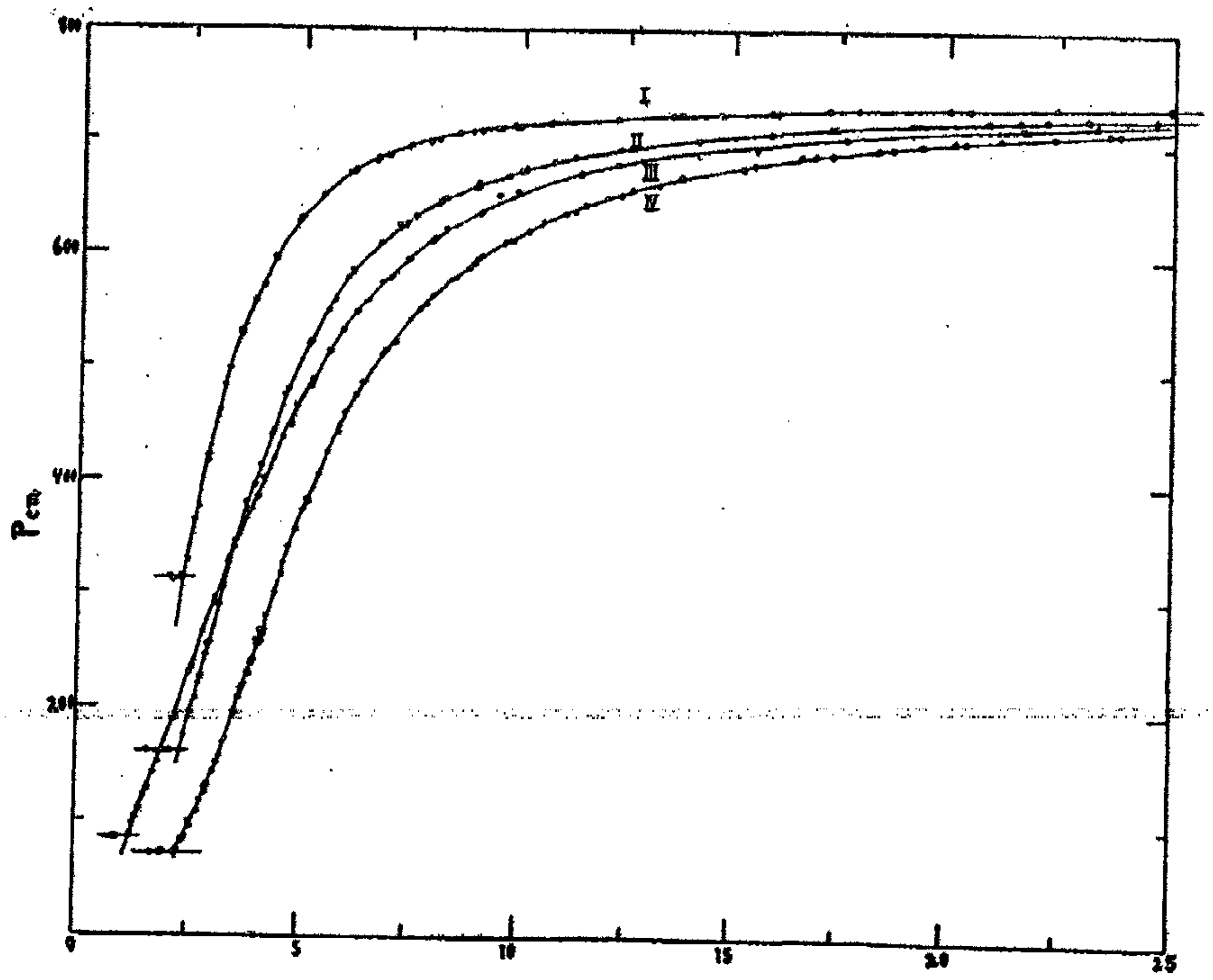
Vapor pressures of ammonium bromide in liquid ammonia at 25°C.

SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4Br}$	P	SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4Br}$	P
		cm. Hg			*cm. Hg*
A	1.56	162.3	C	9.65	671.1
A	1.83	162.3	D	10.7	683.4
B	2.29	162.3	E	12.3	695.1
B	2.50	184.2	E	14.2	704.3
C	2.56	196.5	F	17.5	713.5
C	2.77	226.0	F	21.6	722.2
B	3.00	257.9	F	24.6	725.4
D	3.29	305.5	F	35.1	732.5
C	3.53	340.6	G	39.9	734.9
C	3.93	396.2	F	44.0	735.9
C	4.30	440.1	G	56.3	739.2
C	4.69	480.8	G	71.6	741.5
D	5.17	522.6	H	94.0	743.2
D	5.57	550.7	H	129	745.1
C	5.74	559.7	H	146	745.5
D	6.80	609.0	H	159	745.9
D	7.39	628.1	H	172	746.3
C	9.03	662.5			

TABLE 4

Vapor pressures of ammonium chloride in liquid ammonia at 25°C.

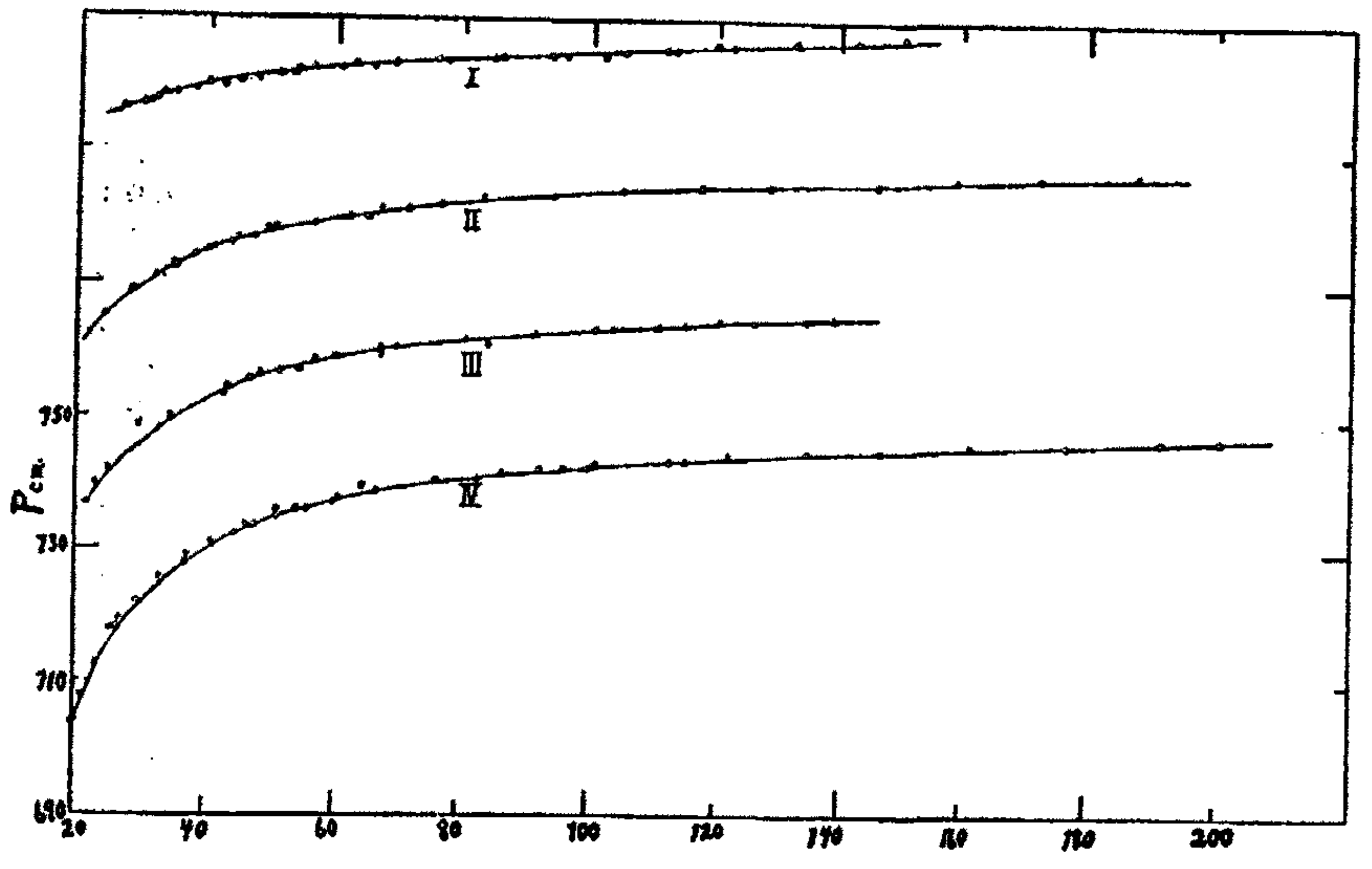
SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4Cl}$	P	SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4Cl}$	P
		cm. Hg			*cm. Hg*
A	2.06	314.0	D	13.8	725.9
B	2.38	314.9	C	16.0	729.0
B	2.62	364.3	D	17.9	730.7
B	2.90	421.2	E	20.0	732.4
B	3.10	456.5	D	24.9	735.2
B	3.37	497.8	D	32.0	737.6
A	3.67	530.3	D	34.7	738.6
B	3.90	558.2	E	51.3	741.7
B	4.32	595.8	F	60.7	742.5
A	4.89	629.0	G	69.0	743.4
A	6.21	674.5	F	86.4	744.2
C	6.71	685.6	G	105	745.2
C	7.48	696.5	F	111	745.5
C	8.55	707.0	G	122	745.9
A	9.41	712.4	G	133	746.8
B	9.96	714.0	G	143	747.1
C	12.2	722.3			



Moles NH_3/Mole Solute

FIG. 3. VAPOR PRESSURES OF SOLUTIONS IN THE CONCENTRATED REGION

I, ammonium chloride; II, ammonium bromide; III, ammonium nitrate; IV, ammonium iodide.



Moles NH_3/Mole Solute

FIG. 4. VAPOR PRESSURES OF SOLUTIONS IN THE DILUTE REGION

I, ammonium chloride; II, ammonium bromide; III, ammonium nitrate; IV, ammonium iodide. Curves I, II, and III have been displaced upward on the ordinate 60, 40, and 20 cm., respectively.

pressed in moles per mole of salt. The tables include only a fraction of the measured pressures.

DISCUSSION OF RESULTS

By this method it is impossible to carry the solutions to the desired dilutions so that we can calculate the activity of the solute. However, we are measuring the freezing points of the dilute solutions and will be able to furnish additional data in a subsequent article.

Since the dielectric constant of ammonia is low, one expects a low activity of the electrolytes in this solvent. However, because of the great proton accepting power of ammonia one expects these ammonia salts to have a high activity. Our vapor pressures indicate that the solute ions are associated in our most dilute measurements. The order of association is what is to be predicted from the magnitude of the ion diameters.

The extremely low concentration of H^+ or protons in (l) NH_3 leads the authors to avoid the term, acids in (l) NH_3, in the usual sense that the term acid is used.

SUMMARY

The vapor pressures of solutions of ammonium nitrate, ammonium chloride, ammonium bromide, and ammonium iodide in liquid ammonia have been determined over as wide a concentration range as possible at 25°C.

REFERENCE

(1) Cragoe, C. S., Meyer, C. H., and Taylor, C. S.: J. Am. Chem. Soc. 42, 206 (1920).

RATES OF COAGULATION. I

AUTOCATALYSIS AND SOL PURITY

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Received November 17, 1933

In a series of studies involving the use of the photoelectric cell as a means of measuring rates of coagulation, Desai (1) and Desai and Patel (2) observed definite evidence of an induction period in the coagulation process. Since the extent of this induction period was found to decrease with increased purification of the sol employed, it seemed pertinent to repeat Desai's studies, using the presumably highly purified sols prepared in this laboratory (4, 5).

The light source used was a 300-watt "Champion" tungsten-filament bulb which was operated on 60 volts at 1.78 amperes. The light from this lamp, which was cooled by placing it in a water bath through which passed a copper coil containing running water, was passed through a lens ($f = 6$ cm.) placed at a distance equal to its focal length from the filament. In series with the lamp were a key, a variable 10-ohm resistance, and an ammeter which could be read to 0.01 ampere. The light, which could be shut off by a shutter placed directly in front of the lens, then passed through a metal tube set in a thermostat to an inner container in the thermostat. Here were placed, in order, a filter of a 2 per cent solution of copper nitrate contained in an optical glass absorption cell (10 × 100 × 100 mm.), the reaction cell (10 × 100 × 70 mm.), also of optical glass, and a photoelectric cell. This last was a product of the General Electric Company (P. J. 23) containing cesium as the sensitive material, which when operated on an anode potential of 90 volts delivered a maximum peak anode current of 5 microamperes.

This current was passed through a Leeds and Northrup wall galvanometer whose sensitivity was 1655 megohms. Readings of the galvanometer deflection were taken on a scale 2.5 meters along its arc, placed at a distance of 7 feet from the galvanometer mirror.

The source of current for the lamp was a bank of storage batteries whose output current was maintained at a constant value by means of the variable resistance mentioned above.

EXPERIMENTAL

Preliminary experiments showed that the ferric oxide sol which was used was not affected by light after an exposure of from three to four hours, and that pure electrolyte solutions were without appreciable effect on the intensity of the transmitted light. Before each determination, a blank was run using 10 cc. of sol diluted with 20 cc. of distilled water in the reaction cell. The necessary time was allowed for all external conditions to become constant and the galvanometer reading was then taken. The zero point was obtained by cutting off the light with the shutter, and the

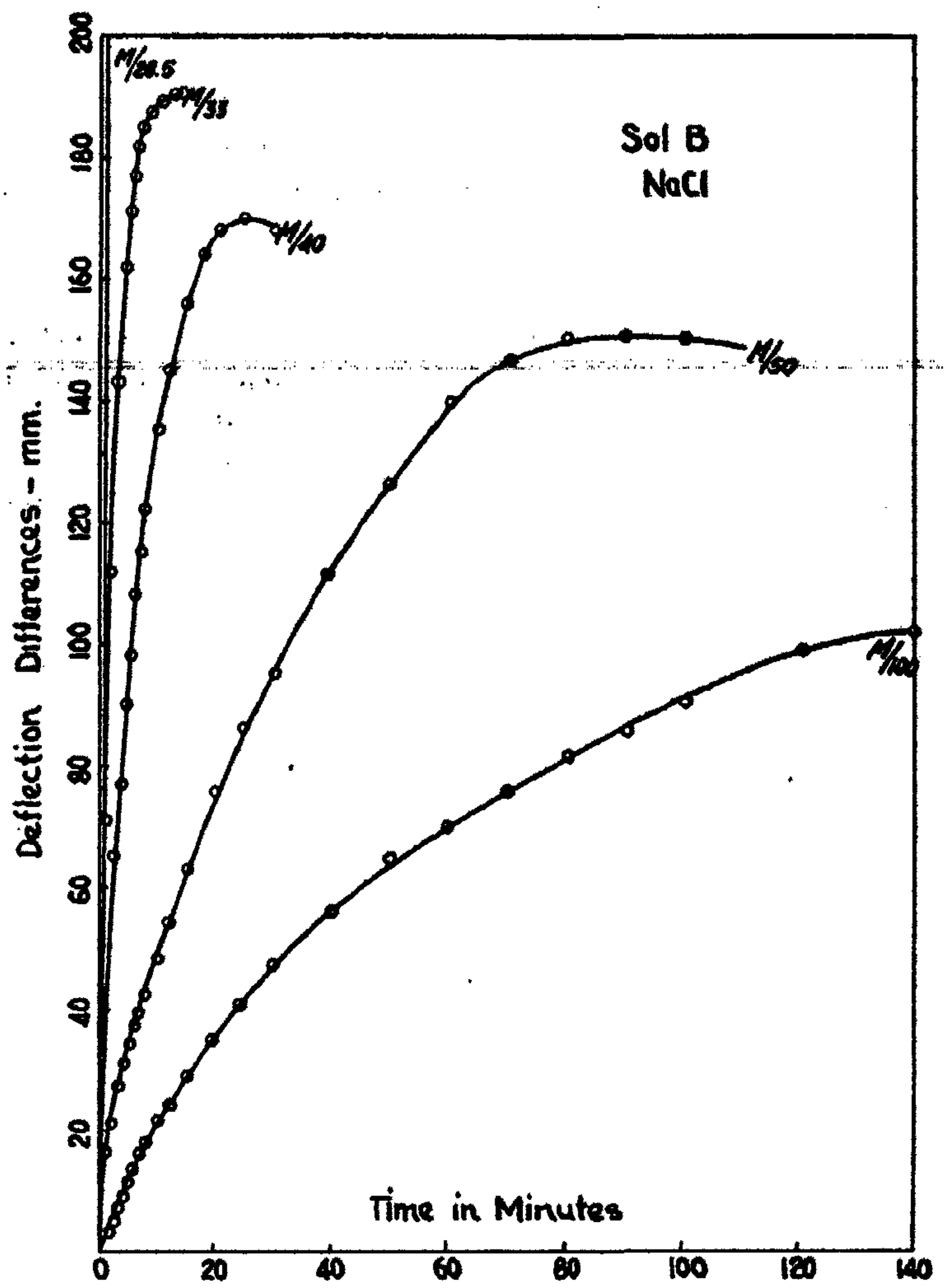

Fig. 1. Coagulation Rates with Sodium Chloride

difference between these two values taken as the standard deflection for the sol under investigation as a measure of the opacity of the pure sol with no added electrolyte.

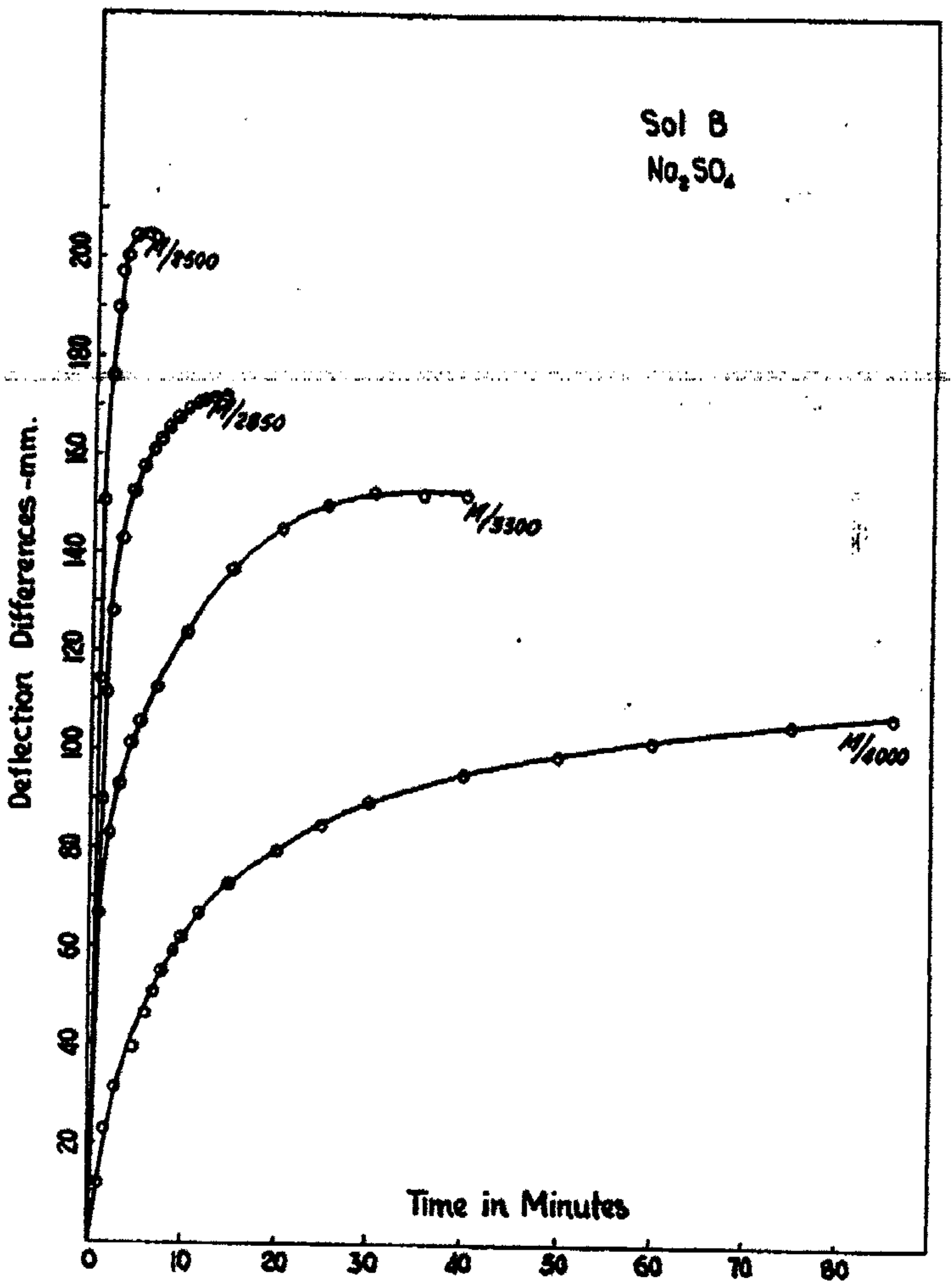

FIG. 2. COAGULATION RATES WITH SODIUM SULFATE

Twenty cc. of electrolyte was then placed in a 125-cc. Erlenmeyer flask, the time taken as being the zero time for the run, and 10 cc. of sol pipetted into the flask. The reaction mixture was then quickly transferred to the reaction cell and the cell placed in its proper position in the inner container of the thermostat. As nearly as possible, the same mixing technique was employed in every determination so as to eliminate any effect due to stirring.

At various times, readings were taken on the galvanometer scale and the differences from the standard deflection plotted against the time, giving the curves shown in figures 1 to 5.

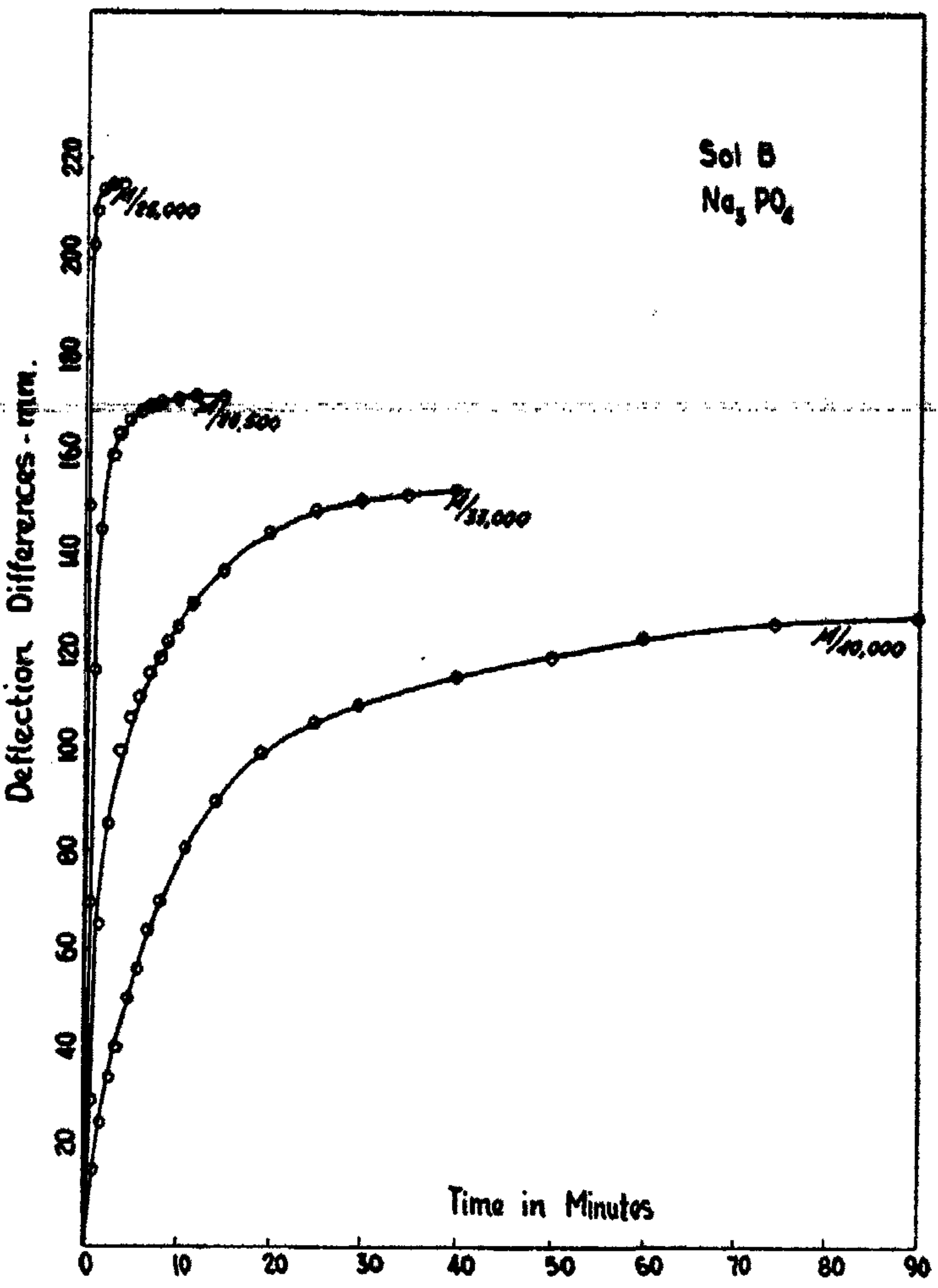

FIG. 3. COAGULATION RATES WITH SODIUM PHOSPHATE

DISCUSSION

Since the decrease in intensity of the transmitted light is a measure of the increase in flocculated sol, the slopes of the various curves give a direct measure of the rate of coagulation at any given time. The plotted results show no induction period; neither do they show any autocatalytic tendency (3).

In all curves there is an evident tendency for the rate to drop off toward the end. Since, in keeping with Desai's technique, the sol-electrolyte mixture was not stirred, this is no doubt caused by a counter-clarification due to sedimentation of the flocculated material. The actual appearance of a floc at the bottom of the cell, and the fact that this dropping off in the rate of decrease of intensity of the transmitted light was more pronounced when the beam of light was shot through the top of the cell and less pronounced when shot through the bottom substantiates this contention.

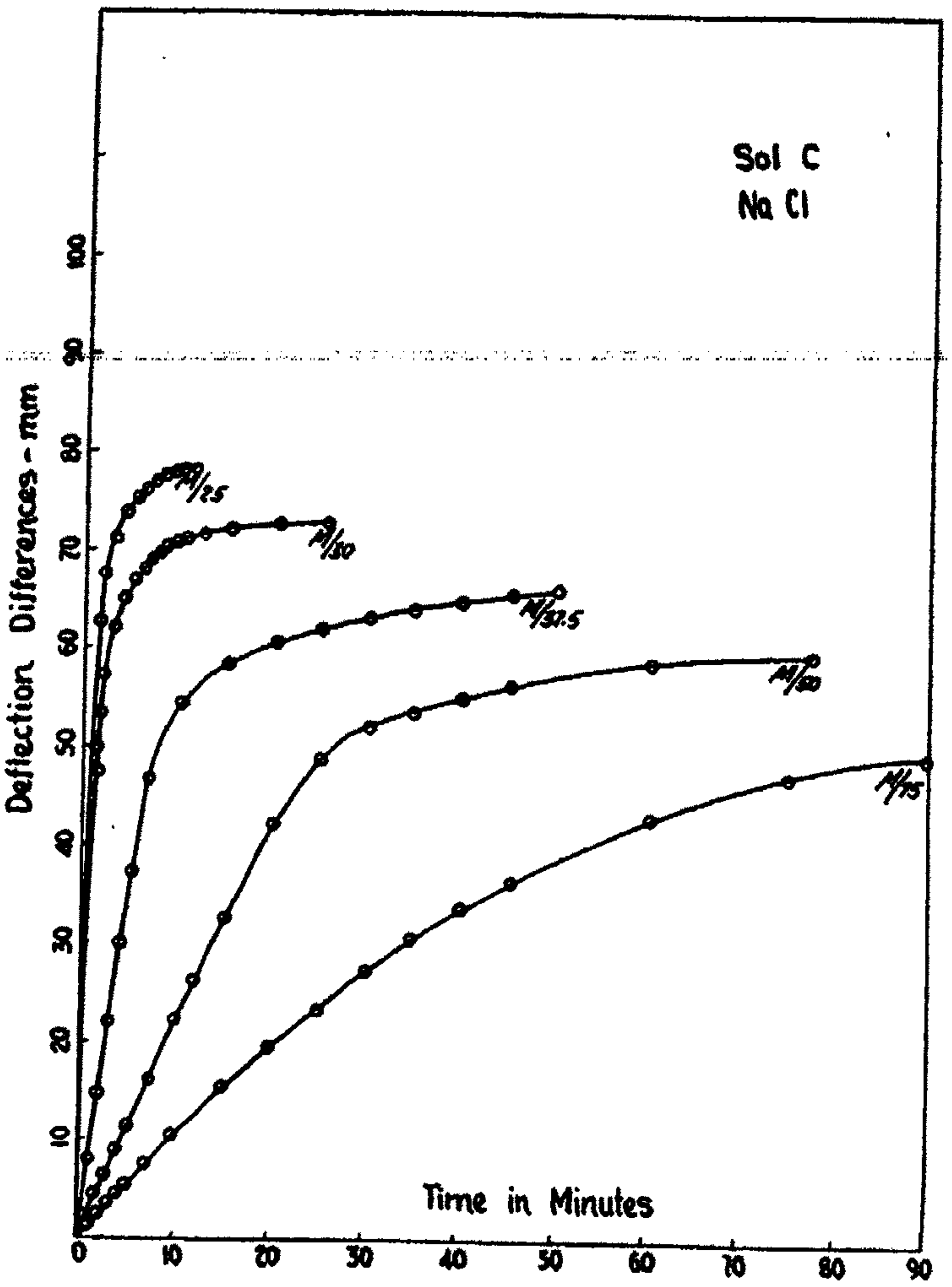

Fig. 4. Coagulation Rates with Sodium Chloride

In view of the fact that agglomeration is presumably the result of colli-

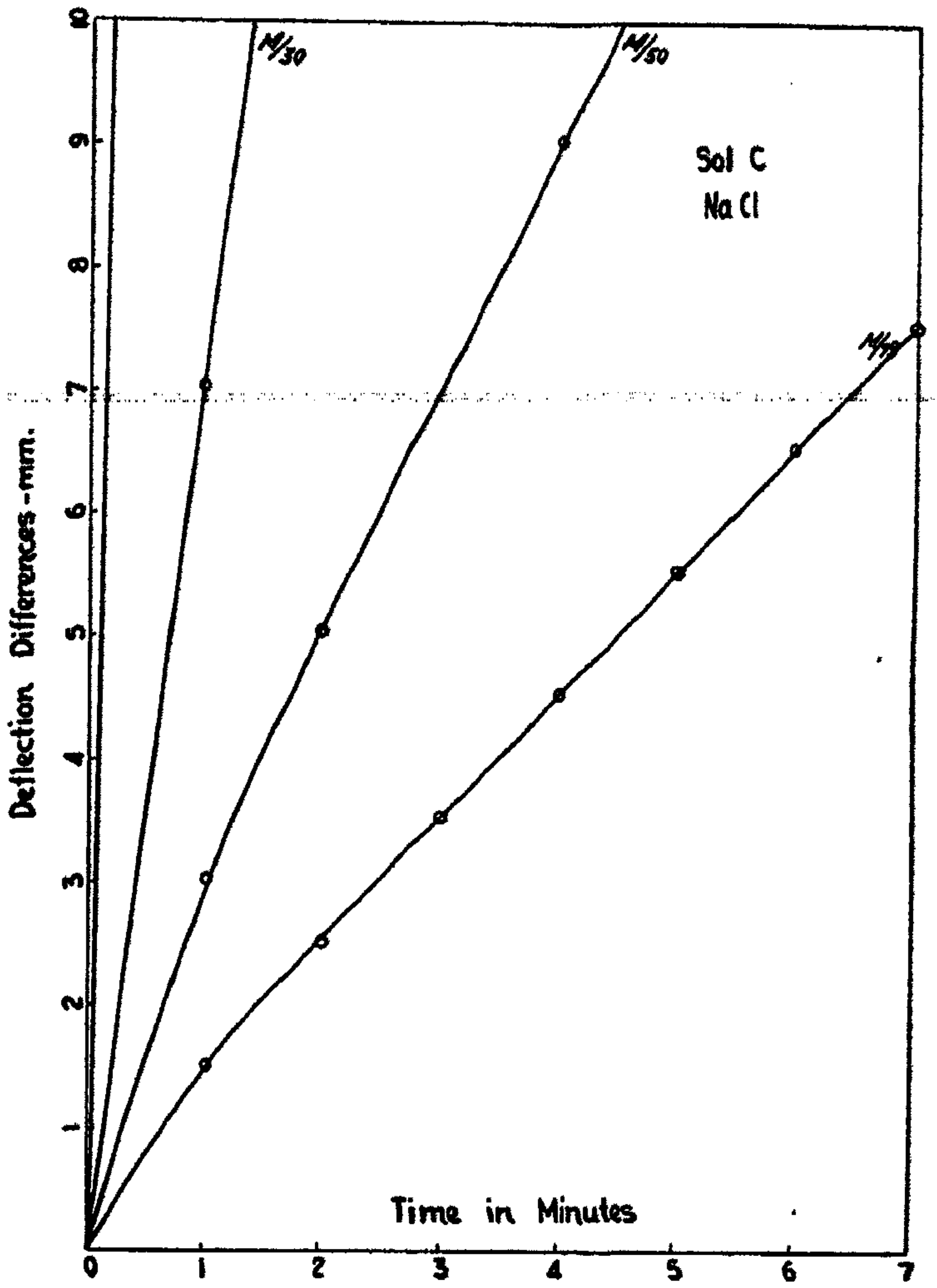

Fig. 5. Coagulation Rates with Sodium Chloride

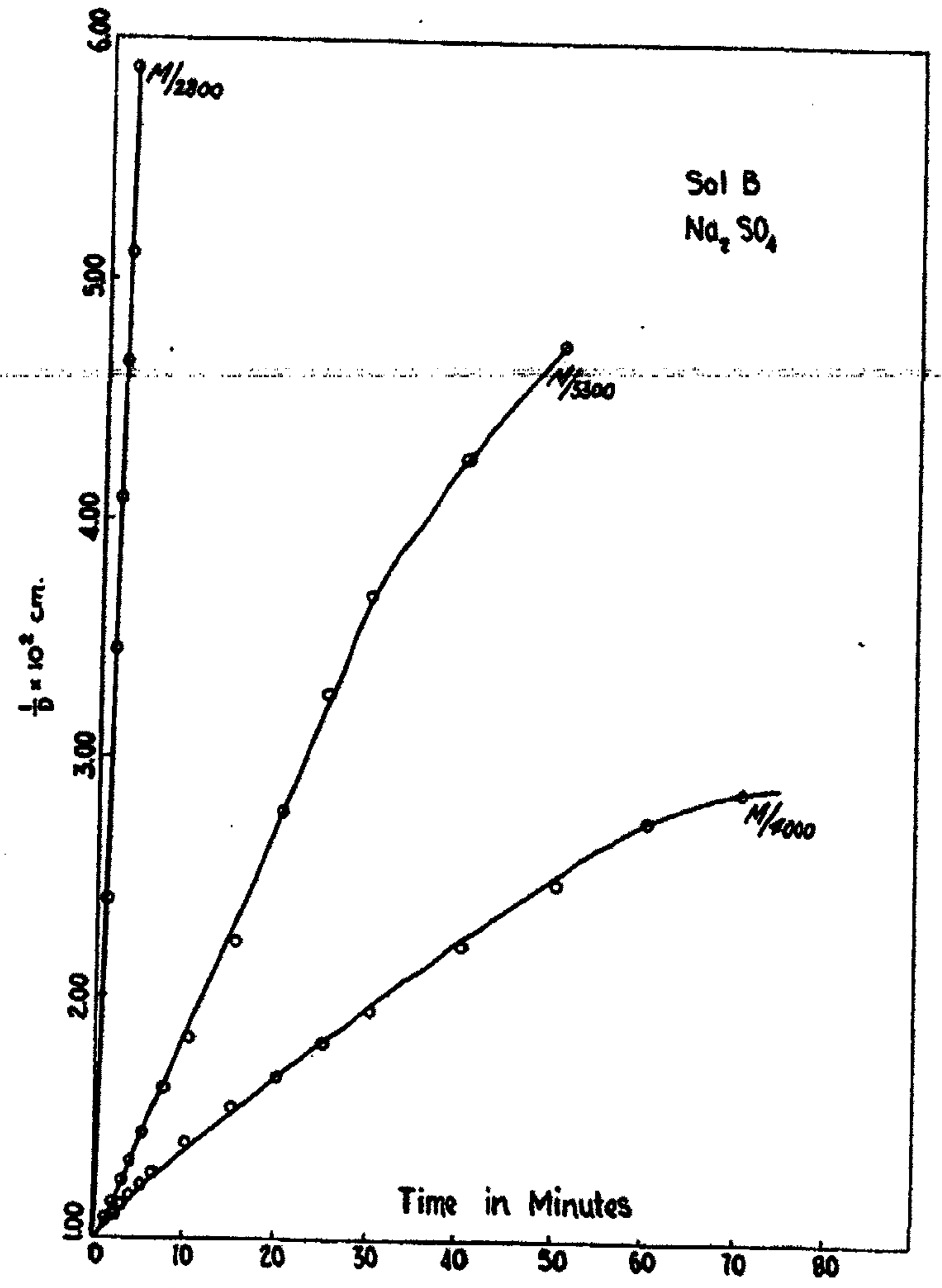

FIG. 6. ORDER OF THE COAGULATION PROCESS

sions between two or more particles, it is to be expected that the reaction might be of second order. In the event that it is second order a straight line should result if the reciprocal of the direct galvanometer reading, which reading is a direct measure of the concentration of unflocculated sol, is plotted against time. Such graphs are shown in figure 6. The results seem to warrant the conclusion that the coagulation process is essentially second order.

The results of studies with stirred sol-electrolyte mixtures will be presented in a later paper.

SUMMARY

1. The rate of coagulation of highly purified ferric oxide sols by various electrolytes has been studied by means of the photoelectric cell using the technique developed by Desai.
2. There is no evidence of an induction period in the flocculation process; the process does not appear to be autocatalytic. This is in agreement with a prediction contained in Desai's experimental results.
3. The flocculation process appears to be essentially of second order.

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(2) Desai and Patel: Trans. Faraday Soc. **26**, 126 (1930).
(3) Mehta and Joseph: J. Indian Chem. Soc. **10**, 177 (1933).
(4) Sorum: J. Am. Chem. Soc. **50**, 1263 (1928).
(5) Sorum: Kolloid-Z. **58**, (3) 314 (1932).

gb. 64

THE TEMPERATURE COEFFICIENT OF PHOTOGRAPHIC SENSITIVITY. I

Low Temperatures and the Natural and Optical Sensitivities of Dyed Silver Halides[1]

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Received January 26, 1934

The primary object of the present study was to ascertain if the natural and the optical sensitivities of dye-sensitized silver halide were sharply differentiated as regards temperature influence. If this were not so, this would be evidence that the mechanism of latent image formation must be very similar in both cases. On the other hand, a very considerable difference, particularly at quite low temperatures, might strengthen the case for those who support a more or less complicated chemical reaction as the basis of optical sensitizing (14).

In discussing previous work on the subject of temperature influence, we regard it as desirable to deal separately, at least for the present, with investigations below normal temperature—i.e., below 20°C.—and those above. Since the experiments to be described in this first part deal with the lower range, discussion of relevant literature will be confined to this interval.

Much of the work on the effect of temperature on sensitivity appears to be rather discordant. Dewar and Abney (4), for example, reported a lowering of 80 per cent in "sensitivity" at -180°C. as compared with that at room temperature, whereas A. and L. Lumière (16) reported that it required 350 to 400 times more exposure to produce the same density on plates exposed at -191°C. as at room temperature, i.e., about 99.7 per cent loss.

Some have found only a slight (if any) change in sensitivity with increasing temperature (21, 22) from -50°C. to $+100$°C., and others a considerable increase (1, 3, 4, 12, 16, 18, 19, 23); some have even found a decrease at the higher temperatures (2, 13).

R. J. Wallace (29), plotting density (less fog) against temperature (from -20°C. to $+100$°C.), found that the lower densities (up to about 1.2) passed through a maximum between -20°C. and 0°C., and decreased more or less for higher temperatures.

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[1] Contribution No. 528 from the Eastman Kodak Co.

The first to notice an effect of temperature on contrast (gamma, or gradation of density with exposure over the normal exposure region, for different development times) was Abney (1). He found that for the most part for exposures with time variation, i.e., intensity constant, temperature variation made little, if any, change on the contrast. With intensity varied and time held constant, he found a lowering of contrast with decrease of temperature between +34°C. and −15°C.

King (13) also mentioned the change of contrast with temperature, but did not say in which direction it trended.

Wallace (29) found that between −10°C. and +20°C. contrast decreased and above 20°C. it remained constant, under the conditions of his experiments. It should be remembered that his results represented sensitometric curves with fog subtracted uniformly for all densities.

Eggert and Luft (5) have tried to explain some of these discrepancies. They found that in plotting the dependence of density for constant energy of (white light) illumination, and (presumably) constant development time, against the temperature, the curve drawn through the observed points had a maximum between −60°C. and −20°C., and a minimum between +40°C. and +60°C., somewhat similar to those of Wallace but at different temperatures. Gammas for the same characteristic curves (for constant development time) from which the densities are taken, decrease to a minimum and then increase again. X-rays, however, produced only a small steady increase in density, for constant energy of illumination, with temperature increase.

One cause for the lack of agreement among the various investigators as to the effect of temperature change on photographic sensitivity has been the looseness with which the word "sensitivity" has been used. It has had distinctly different meanings with different workers. We shall use the term to imply the average relative sensitivity of all the silver halide grains of the plate, as modified by their surroundings of gelatin, etc., the relative sensitivity of the individual grains being defined as the exposure (to some standard light source) just sufficient to make the grain developable under some chosen standard conditions of development, which takes into account the developer, the temperature, and the time of development.

We shall use the term "speed" to mean $10 \times 1/i$, i being the inertia of the plate, or that exposure on the log E axis at which the straight-line portion of the D-log E curve extended cuts the axis. This is often called the H. and D. speed, although Hurter and Driffield used a different factor than 10.

Another cause for the discrepancies in conclusions concerning the effect of temperature lies in the fact that no two investigators used the same sensitometric procedure. The conclusions were derived from very meager data, frequently from just two or three exposures and one development time, the conditions of exposure and development not being specified, nor the type of plate used.

Even more important, as indicated by recent unpublished investigations by Dr. J. H. Webb, of the Physics Department of this Laboratory, is the intensity level. Since our results were obtained with a mixed régime, i.e., an intensity scale of exposures instead of a time scale, they can only be regarded as comparative, but we regard them as significant for the comparison of natural and optical sensitivities.

This investigation is by no means complete, having been conducted so far at only three temperatures, −180°, −70° and +20°C., and with comparatively few different kinds of plates, but results have already been obtained which it was felt warranted publication.

EXPERIMENTAL PROCEDURE

The plates which were cooled to −70°C., and their controls at room temperature, were exposed in a vertical sensitometer in which they lay on a metal box, in a metal drawer. The temperature of the box was lowered by partly surrounding it with solid carbon dioxide, and by passing through it acetone cooled by allowing it to flow through a copper coil packed in solid carbon dioxide in a surrounding vessel. The system was well insulated, and was provided with a means of raising the acetone back from a lower reservoir into an upper reservoir after the latter had emptied itself.

The temperature at the surface of the plate was determined by pressing against it a calibrated alumel–chromel thermocouple, connected with a galvanometer and rheostat, the former having a scale graduated in tenths of a millivolt, and which could easily be estimated to 0.1 to 0.2 millivolt. The thermal junction was flattened so as to make as intimate contact with the plate as possible.

The calibration was carried out by burying the thermocouple in liquid nitrogen, liquid oxygen, solid alcohol, solid ethyl chloride, solid carbon dioxide, a soft mush of carbon dioxide in acetone, salt and ice in water, pure ice in water, and water at various temperatures above 0°C. up to 60°C.

As the room temperature was fairly constant, in the neighborhood of 20°C., the refinement of operating the above thermocouple against a standard at, say 20°C., was found unnecessary, although the room temperature was recorded.

A curve of the galvanometer readings plotted against temperature was drawn, and found to be practically a straight line above −80°C.

There was no appreciable condensation of moisture on the plate when placing it in the sensitometer nor during the period it remained there, since practically all moisture inside the sensitometer was displaced by the rapidly evaporating carbon dioxide.

The same sensitometer was used for attaining exposures at −180°C., but the cooling system was modified, in that liquid air was passed directly from its upper container through an insulated tube to the metal box which was partly surrounded by either liquid air or liquid nitrogen, and from the metal box to a lower container, and the whole system was more thoroughly insulated.

The temperature of a plate lying on the metal box when the latter was surrounded with liquid nitrogen was very little, if any, different from that when liquid air was used as the surrounding medium, because liquid air was flowing rapidly through the inside of the box all the while.

The difference in speed and in contrast at −180°C. (noted below), when liquid nitrogen was used around the box in the drawer, as compared with liquid air, was therefore not due to temperature difference but perhaps to the presence of a small amount of ozone in the oxygen vaporized from the liquid air. The ozone would no doubt react with the dye in the panchromatic plate, which, it was observed, does very quickly lose its orchid color in the vapor above liquid air, even without the action of light. Dewar has shown that liquid air, when evaporating, does form some ozone, especially when acted on by light (4).

Because the rubber tube connections would become hard and brittle at that low temperature, the metal drawer containing the metal box was fastened securely to supports screwed to the work bench, and the sensitometer was put on a platform on wheels and rolled back and forth to open and close it.

The sensitometer itself (27) consisted of a balopticon with a short-focus lens, which focused, for the desired time, the image of a step tablet onto a 4 x 5 inch plate lying on the metal box in the metal drawer, by opening and closing a metal flap in front of the lens. The exposure time was either 1 minute or 2 minutes.

The light from the sensitometer lamp (which was operating at about 110 volts) before reaching the plate, passed through filters. With panchromatic plates, either a Wratten No. 39 glass filter + a 15 per cent copper sulfate solution in a 1-cm. deep glass cell, or a Wratten No. 9 + a Wratten No. 29 gelatin filter were used to give *blue-violet* or *red* light, respectively. The former combination has a maximum transmission at about 380 mμ to 400 mμ and no transmission of wavelengths longer than 510 mμ. The latter filters cut off all light of wavelength shorter than 600 mμ. With the process plates, not dye-sensitized, we substituted for the red filter a Kodak No. 4 filter, transmitting only beyond 480 mμ.

After the exposure at the low temperature, the plate was placed in a 4 x 5 inch plate box. Of course, some moisture condensed on it in trans-

TABLE 1

Comparison of relative speeds of panchromatic plates for blue-violet and red light at different temperatures with pyro–soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF									AVERAGE SPEED
			2 min.	3 min.	4 min.	6 min.	10 min.	15 min.	20 min.	30 min.	60 min.	
		degrees C.										
Control	Blue-violet	+20	479	417	417	417	417	417	417	(417)*	—	425
	Red	+20	324	324	324	324	324	324	324	(324)	—	324
Solid carbon dioxide	Blue-violet	−70	363	288	288	316	692	—	—	—	—	389
	Red	−70	229	229	229	263	331	—	—	—	—	256
Liquid nitrogen	Blue-violet	−180	39	39	39	39	50	(51)	(53)	55	23	43
	Red	−180	11	12	8.3	12	12	10	(10)	10	10	10.6
Liquid air†	Blue-violet	−180	22	25	25	25	28	28	(29)	30	—	27
	Red	−180	—	—	35‡	17	8.7	8.7	(8.7)	8.7	—	10.4

* Parentheses indicate interpolated or extrapolated values.

† Differences between liquid air and liquid nitrogen, which are particularly notable with panchromatic plates, are probably due to certain amounts of bleaching of dyes by ozone from the liquid air.

‡ These values not included in the averages.

TABLE 2

Comparison of relative speeds of panchromatic plates for blue-violet and red light at different temperatures using p-aminophenol developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF								AVERAGE SPEED
			3 min.	4 min.	6 min.	10 min.	15 min.	20 min.	30 min.	60 min.	
		degrees C.									
Control	Blue-violet	+20	562	513	339	339	309	309	(378)	447	400
	Red	+20	316	316	316	363	363	251	251	—	311
Liquid air	Blue-violet	−180	—	—	47.0	118	—	118	47.0	—	83
	Red	−180	—	—	17.4	17.4	—	17.4	(17.4)	—	17.4

ferring it to the box, but this, it was known from previous experiments on the effect of moisture on the sensitivity and latent image (27), had no appreciable effect on the latter. The plate was not developed until it had attained room temperature again and the moisture had evaporated.

The plate which had been cooled was developed along with an uncooled one which had previously been exposed in the sensitometer at room temperature (about 20°C.) (or in some cases with one which had been cooled after exposure) in a standard pyro-soda developer[2] at 20°C. Development time was varied from 2 minutes to 60 minutes. Some experiments were also done using *p*-aminophenol developer.[3]

EXPERIMENTAL RESULTS

The full results are best presented as the actual sets of characteristic curves obtained at each temperature and for all times of development, but this is likely to be regarded as taking too much space. We give, therefore, tables of sensitometric variables taken from these curves, as well as graphs derived from these. In tables 1 to 3 are given the data on total speeds[4] at 20°C., −70°C., and −180°C. for Wratten panchromatic

TABLE 3

Comparison of relative speeds of process plates for blue-violet and bluish green-yellow light at different temperatures using pyro-soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF		AVERAGE SPEED
			2 min.	6 min.	
		degrees			
Control	Blue-violet	+20	84	89	87
	Green-yellow	+20	11.5	12.6	12
Liquid nitrogen	Blue-violet	−180	5.3	3.4	4.4
	Green-yellow	−180	0.63	0.63	0.63

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[2] Standard pyro-soda developer:

Solution A:		Solution B:	
Na_2SO_3 (anhydrous)	256 g.	Na_2CO_3 (anhydrous)	300 g.
$NaHSO_3$	70 g.	KBr	4 g.
Pyrogallol	80 g.	Water to	4 l.
Water to	4 l.		

[3] Standard *p*-aminophenol developer:

p-Aminophenol hydrochloride	7.275 g.
Na_2SO_3 (anhydrous)	50. g.
Na_2CO_3 (anhydrous)	50. g.
Water to	1. l.

[4] Not subtracting fog. For practical photographic purposes, "speed minus fog" or a similar value, is more useful, but not for sensitivity studies.

plates, with *blue-violet* and *red* radiation, respectively, with both a pyro-soda, and a *p*-aminophenol developer, as also the value of γ (gamma), the slope of the characteristic curve. Data are also given for a process plate for *blue-violet light* (maximum at 380 mμ to 400 mμ) and for bluish green-yellow rays longer than 480 mμ, of which only the shorter ones are effective. These represent data on wavelength effect *within* the natural absorption region of the silver iodobromide, and not for optically (dye) sensitized material.

TABLE 4

Wratten panchromatic plate

TEMPERATURE	SPEED NUMBERS	
	Blue-violet	Red
	Pyro-soda developer	
degrees C.		
20	425 ≃ 100 per cent	324 ≃ 100 per cent
−70	389 92	256 79
−180 (Nitrogen)	43 10	10.6 3.5
−180 (Air)	27 6.3	10.4 3.3
	p-Aminophenol developer	
20	400 ≃ 100 per cent	311 ≃ 100 per cent
−180 (Air)	83 20	17.4 5

Process plate

TEMPERATURE	<480 mμ	<480 mμ
	Pyro-soda developer	
degrees C.		
20	87 ≃ 100 per cent	12 ≃ 100 per cent
−180 (Nitrogen)	4.4 5	0.63 5

The average values of the relative speeds are collected and reduced to a percentage basis in table 4. It will be noticed that while the fall in speed—and consequently in threshold sensitivity—is comparatively small from 20°C. to −70°C., it becomes very considerable, both for the natural and the optical sensitivity, from −70°C. to −180°C. The results for the Wratten panchromatic plates appear to indicate that the optical sensitivity ("red") falls off considerably more than the natural or blue-violet values. But this cannot be regarded as proven by these data, because the values for the blue-violet sensitivity at −180°C. are rather widely scattered, namely as follows:

Panchromatic plates at −180°C.

Pyro	Nitrogen	10.0 per cent of 20°C. speed (blue-violet)
Pyro	Air	6.3 per cent of 20°C. speed (blue-violet)
P. A. P.	Air	20.0 per cent of 20°C. speed (blue-violet)

Process plate

Pyro	Nitrogen	5 per cent of 20°C. speed

Also, there are no data on process plates cooled in the presence of liquid air or developed in p-aminophenol.

TABLE 5

Comparison of gammas of panchromatic plates for blue-violet and red light at different temperatures, with pyro–soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF							
			2 min.	3 min.	4 min.	6 min	10 min	15 min.	20 min.	30 min.
		degrees C.								
Control	Blue-violet	+20	0.52	0.85	1.12	1.45	1.84	2.16	2.67	—
	Red	+20	0.64	1.09	1.53	2.08	3.10	3.72	4.00	—
Solid carbon dioxide	Blue-violet	−70	0.33	0.56	0.67	1.00	1.17	—	—	—
	Red	−70	0.40	0.66	0.81	1.15	1.68	—	—	—
Liquid nitrogen	Blue-violet	−180	0.15	0.28	0.42	0.68	1.07	1.30	—	1.85
	Red	−180	0.15	0.25	0.43	0.62	1.13	1.62	—	2.10
Liquid air	Blue-violet	−180	0.09	0.18	0.25	0.44	0.81	0.93	—	1.55
	Red	−180	—	0.06	0.17	0.27	0.63	0.84	—	1.37

Hence it does not appear possible to conclude that the optical sensitivity is much more depressed than the natural (blue-violet) sensitivity, in so far as threshold sensitivity is concerned.

A more definite distinction between the blue-violet and red light-exposed plates appears in regard to contrast (γ_∞) and perhaps maximum developable density (D_{max}) which would be an approximate measure of the total photographic "yield." The data (tables 5 to 8) indicate that for the blue-violet there is no considerable fall of γ_∞ or D_{max}, but chiefly a shift of inertia with lowered temperature. With the "red" light, however, there appears to be a progressive reduction of γ_∞, with possibly some fall of D_{max} (cf. table 8). If it were quite correct that there were no fall of γ_∞ with lowered temperature for "blue-violet" light (*i.e.*, with fall of

TABLE 6

Comparison of gammas of panchromatic plates for blue-violet and red light using p-aminophenol developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF							
			3 min.	4 min.	6 min.	10 min.	15 min.	20 min.	30 min.	60 min.
		degrees C.								
Control	Blue-violet	+20	0.62	0.83	1.20	1.54	1.89	2.08	—	2.21
	Red	+20	1.01	1.46	1.74	2.56	2.83	3.06	3.90	—
Liquid air	Blue-violet	−180	—	—	0.25	0.31	—	0.54	0.75	—
	Red	−180	—	—	0.21	0.32	—	0.48	—	—

TABLE 7

Comparison of gammas of process plates for blue-violet and green-yellow light at different temperatures using pyro–soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF	
			2 Min.	6 Min.
		degrees C.		
Control	Blue-violet	+20	1.67	3.48
	Green-yellow	+20	1.90	4.36
Liquid nitrogen	Blue	−180	0.37	1.51
	Green-yellow	−180	0.30	1.14

TABLE 8

γ_∞ for panchromatic plates at various temperatures with blue-violet and red light

COLOR OF LIGHT		γ_∞			
		At 20°C.	At −70°	At −180° l.N.	At −180° l.a.
Blue-violet	(a)	2.13	—	1.53	1.42
	(b)	2.52	1.56	2.72	2.67
	(c)	2.93	—	2.56	2.70
Red	(a)	4.49	—	2.17	1.13
	(b)	5.04	3.28	3.49	1.82
	(c)	4.46	—	2.61	1.26

(a) Values in this row determined from equation $d\gamma/dt = k(\gamma_\infty - \gamma)$ and intermediate values of gamma are approximately constant.

(b) Values in this row determined from the above equation with $\gamma = 0$.

(c) Values in this row determined from the above equation with γ for 30 minutes development time, except those at −70°C., which were obtained with γ for 10 minutes development time.

natural sensitivity) then the general results could be diagrammatically represented as in figure 1. This would mean that as regards "blue-violet" radiation, all grains, of whatever initial size and sensitivity, were equally reduced in sensitivity (causing a parallel shift in the characteristic curve).

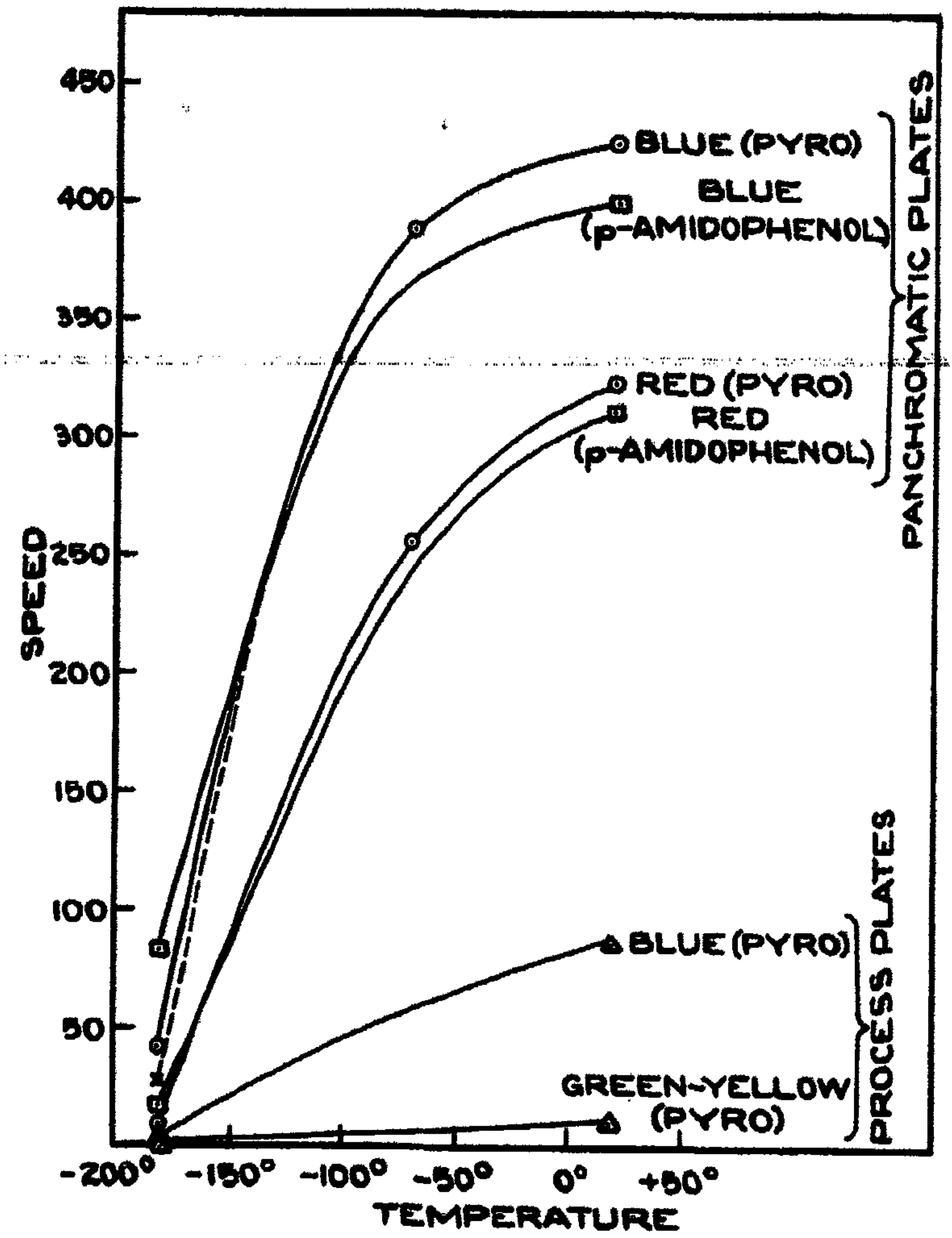

Fig. 1. Effect of Temperature on Speed

There is some evidence against this in the somewhat larger speed reduction of the process (slower, fine-grained plate) than of the panchromatic plate. But the influence of "desensitization" on the temperature coefficient remains to be specifically investigated. Provisionally, all that one can say is that there seems to be less tendency to diminution of sensitivity at very low temperatures for the natural (blue-violet) sensitivity than for the optical (dye) sensitivity, for the most sensitive grains, but that the changes in sensitivity become of the same order for the grains of lower sensitivity.

DISCUSSION

We may summarize the principal results of the investigation in the form of four propositions, and then consider possible interpretations of these.

1. There is a relatively small drop in sensitivity, both natural and optical, from 20°C. to −70°C.
2. There is a large drop in both cases from −70°C. to −180°C.
3. Even at −180°C. there persists some 5 per cent or more of the original threshold sensitivity at 20°C.
4. Latent image formation by red light in optically (dye) sensitized grains seems to be affected by very low temperatures similarly to the process in grains of low sensitivity with blue-violet light.

Effect on absorption

According to Fesefeldt and Gyulai (7), to Fesefeldt (6), and to Hilsch and Pohl (11) the ultra-violet and violet absorption of silver chloride is very little affected, about 5 per cent by a temperature of −180°C. On the other hand, Toy and Harrison (28) give values for the absorption coefficients of silver bromide at −180°C. showing a much larger decrease in absorption, viz., about 75 per cent at 365 mμ, 59 per cent at 406.2 mμ, and 45 per cent at 435.8 mμ. Between 20°C. and −180°C. they found the decrease in direct proportion to the temperature drop.

Hilsch and Pohl (11) state that the absorption spectra of the color centers (produced by ultra-violet illumination) in silver chloride and silver bromide crystals were unaffected (within probable experimental error) by temperatures down to −180°C. *If* the absorption of silver bromide is more affected by temperature drop than that of silver chloride, it is possible that that of silver iodide would be still more seriously reduced, and even that of silver iodobromide more than that of pure silver bromide. However, the small effect of a temperature drop to −180°C. on the absorption of thallium bromide and thallium iodide observed by Fesefeldt (6) makes any such large changes as those given by Toy and Harrison seem doubtful. Hilsch and Pohl speak, in fact, in general terms of "the practical temperature independence of the absorption spectra of the silver halides." It may be doubted, therefore, whether change of absorption contributes materially to the fall of photographic sensitivity of the non-optically sensitized silver halide.

In the case of dye-sensitized material, it is the absorption of the adsorbed dye which is in question. We have not found much information in the literature on the effect of low temperatures on the absorption by dyes, at least in the solid state, which is the nearest to that concerned. The investigations of Königsberger and Kilching (15) were concerned with temperatures from 20°C. upward. For dyes such as fuchsin, cyanin, iodeosin—sufficiently near in type to sensitizing dyes—they concluded: (1) that absorption in the visible spectrum is due to one resonating electron per molecule; and (2) that for a rise of 75°C. the maximum was displaced some 8 mμ toward the longer wavelengths, and only slightly weakened and broadened.

The inference would be that, as found with other materials, lowering the temperature to say −180°C., might displace the absorption maximum about 10 to 20 mμ toward the shorter wavelengths, and somewhat narrow the absorption band. On this basis, there appears no reason to expect so large a lowering of total red sensitivity as was actually found.

Primary and secondary processes

Regarding the primary process, in the case of the silver halide, as the absorption of light and, to a first approximation, as

$$\mathrm{Br}^- + h\nu \longrightarrow \theta + \mathrm{Br}$$
$$\mathrm{Ag}^+ + \theta \overset{\swarrow}{\longrightarrow} \mathrm{Ag}$$

the parallel event for the dye would be

$$D + h\nu \longrightarrow \theta + D^1$$

where D^1 represents an unsaturated radical derived from the dye molecule, which can, for example, couple to form with another D_2, just as dianthracene is formed from anthracene on exposure to ultra-violet light[5] (17, 20).

$$\mathrm{A} + h\nu \longrightarrow \theta + \mathrm{A}^1$$
$$\mathrm{A}^1 + \mathrm{A}^1 \longrightarrow \mathrm{A}_2$$
$$\mathrm{Ag}^+ + \theta \longrightarrow \mathrm{Ag}$$

Since neither of these photoelectronic processes would be much affected by temperature change, we must look for the carrier of the temperature effect in secondary processes of latent image formation:

1. In the case of ultra-violet and blue-violet sensitivity (natural absorption by silver halides) this might be a greater regression of latent

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[5] The mechanism suggested for these photopolymerizations is that of an internal photoelectric effect. Both anthracene and the sensitive dyes show external photoelectric effects in the shorter ultra-violet, and the dyes (cf. A. Goldmann: Ann. Physik [4] 28, 449 (1908)) give photovoltaic effects in aqueous systems for light in their visual absorption bands.

image after low temperature exposures, by bromine. Thus, conceivably at higher temperatures, the bromine atoms formed are very rapidly removed, whether by interaction with gelatin or other halogen acceptor. It is feasible that at very low temperatures, not merely is this reaction suspended, the bromine atoms being frozen in *statu nascendi*, but that on return to normal temperatures the bromine has a greater probability of attacking the latent image silver atoms. Certainly in one respect a difference would exist. Any bromination (or halogenation) occurring *in light* at normal temperatures would be partly a photobromination; such photobrominations have notoriously high temperature coefficients for photochemical reactions (8). In any event, the possibility exists that retarded halogen acceptance may account for the considerable fall of sensitivity of non-optically sensitized silver halide.

However, it appears more difficult to account in this way for the equal or greater fall in dye-induced optical sensitivity, since there is no evidence that in this case any halogen is actually liberated. It would require very complicated and rather improbable mechanisms to ensure that the light absorbed by the dye molecule should not only release an electron from a halide ion, but also, and necessarily, pass this on to a silver ion.

2. An alternative secondary process is that involved in aggregating or *concentrating* sufficient silver atoms produced by the primary process to form a nucleus capable of inducing development. On the orientation theory of "concentration specks" (25) it is supposed that silver sulfide specks in the grain induce or orient the reaction

$$Ag^+ + \theta \rightarrow Ag$$

to occur at the interface Ag_2S : Ag Hal. Whether the whole quantum event

$$Br^- + h\nu \rightarrow Br + \theta + Ag^+ \rightarrow Br + Ag$$

is thus oriented, or only the part reaction above, is not implied in the theory. An essential corollary to this is that as far as the natural absorption is concerned, the whole projective area of the grain is the receptive or working area (25). This has recently received confirmation from experiments by J. H. Webb on the reciprocity failure (30).

The studies on photoconductance in the silver halides by Toy and Harrison (28), and by Harrison (10), as well as those on the photovoltaic effect with silver:silver halide electrodes by Sheppard and Vanselow (26) indicate that the photoelectrons in silver halide crystals can traverse quite considerable distances. Gudden and Pohl (9) point out that this is characteristic of crystals with high refractive index, in which the potential barriers between adjacent ions are not so steep as those in purely ionic lattices, such as the alkali halides. In any case, the orientation hypothesis presupposes a system of energy slopes, or potential gradients, in the crystal focusing upon the speck. It appears feasible that at very low temperatures this system is altered, that the lattice becomes more like that of the alkali halides, so that orientation of the photo-effect becomes increasingly difficult,—which would be equivalent to a progressive desensitization by reduction of receptive area.

The data on the effect of low temperatures on photoconductance (10, 28), are too variable to throw much light on this. They do show, however, that the thermal history of the crystal, and its consequent structure, greatly affect the temperature coefficient.

It seems possible that further insight into the nature of the sensitivity drop at very low temperatures may be obtained, e.g., by examining the effect for x-rays or α-particles. This is *independent* of sensitivity nuclei, and only determined by the projective area (24). Again, the temperature coefficient of chemically desensitized plates should be compared with that before desensitization. Work on these phases is under way.

Density measurements and much of the development in the work here reported was carried out by Mr. E. Huberth, to whom we wish to express our thanks.

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STUDIES ON GLASS. IX

THE ELECTRICAL CONDUCTIVITY OF BORON TRIOXIDE–SODIUM BORATE GLASSES[1]

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Received November 24, 1933

It has been shown quite conclusively that the conduction of an electric current by certain glasses is due to the transference of ions (5). In other glasses, however, such as those composed of very simple inorganic and complex organic molecules, it is difficult to decide on the nature of the charge carriers.

Schönborn has presented data on certain borosilicate glasses which conduct ionically (3). His measurements show a definite break in the conductivity–temperature curve at a point corresponding to the softening region of the glass.

With boron trioxide, however, no evidence of such a change in the transition region has been reported (4, 6). Various boron trioxide–sodium borate systems have also been measured, but these too showed no irregularities.

This investigation represents a further study on boron trioxide–sodium borate (B_2O_3—$Na_2B_4O_7$) systems, undertaken and carried out with the aid of a new and highly refined method of measurement.

APPARATUS AND PROCEDURE

The apparatus used to make the conductivity measurements was a modification of that described by Clark and Williams (1). The modifications were introduced in the interests of greater sensitivity and ease of control. The circuit was essentially a modified Wheatstone bridge employing precision standard resistances, variable potentials on two of the bridge arms, and a high-sensitivity quartz-suspension Compton electrometer.[3]

For measurements on pure boron trioxide and mixtures containing small percentages of sodium borate, a conductivity cell was constructed of Monel

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[1] This work is a contribution to the series of studies on glass which are being conducted by Professor George S. Parks at Stanford University.

[2] Shell Research Fellow at Stanford University, 1932–1933.

[3] The refinements of the apparatus over that described by Clark and Williams (1) will be reported by one of us (J. D. C.) at a later time.

metal. The outside was turned to fit a cavity in a large electrically heated copper block. In the center of the Monel piece, a cylindrical cavity of 10.5 mm. diameter and 50 mm. depth was drilled. A piece of silver wire was connected with this container, which then served as one electrode. The other electrode was a Monel rod (6.80 mm. in diameter) extending through a hole in a copper plug which was turned to fit tightly in the cone top of the copper-block cavity. This electrode was insulated from the copper plug by means of two pieces of Pyrex tubing, one fitting inside the other, the Monel rod fitting inside the smaller one, and the outer one fitting into the hole drilled through the copper plug. The inner electrode was thereby concentric with the cavity in the container, leaving a space of 1.85 mm. between the two cylindrical surfaces.

The cell constant for the two concentric cylinders, neglecting the effect of the end surface of the rod,[4] is evaluated by the following equation:

$$\bar{\mu} = \mu \frac{\ln r_2/r_1}{2\pi L}$$

where $\bar{\mu}$ = specific conductivity, μ = reciprocal of measured resistance, and L = length of lateral exposure of the inner electrode.

For measurements on pure borax and mixtures containing high percentages of borax, the glass samples were blown in the form of tubes sealed at one end, having an outer diameter of about 1 cm. and an inner diameter of about 0.8 cm. The inner electrode consisted of a liquid sodium amalgam which was used as the anode. The tube containing the sodium amalgam was immersed in mercury, which served as the other electrode. A small electrically heated oven was used for temperature control. The cell constant was calculated in a manner similar to that above.

Temperatures were measured with a carefully calibrated noble-metal thermocouple and a White potentiometer. The thermocouple junction was inserted adjacent to the conductivity cell.

The samples of boron trioxide were prepared by heating in a platinum crucible at a temperature of 1200–1500°C. for one to two hours. The boron trioxide–sodium borate mixtures which were measured in the Monel cell were prepared by fusing the two components at the above temperature until all ebullition had ceased. While in a fluid condition, the sample was poured into the Monel container. The container was then heated to 600–700°C., placed in the copper block, and the inner electrode was immersed while the glass was still very hot. The system was brought to thermal balance at about 350°C. and measurements started at that point. The sample was then heated and cooled repeatedly over the temperature interval studied.

[4] A thickness of material between the end surface and the outer electrode was used such that a consideration of this effect is not necessary.

The glass tubes were prepared by heating and blowing to the desired shape.

EXPERIMENTAL RESULTS

Two samples of boron trioxide glass were first measured from 370°C. down to 130°C. Next, three boron trioxide glasses diluted with sodium borate were measured over a similar temperature interval using the Monel cell. The percentages of sodium borate present were 2.68, 5.42, and 16.74. As a check on the consistency of the procedure, another pure boron trioxide sample was measured at this point. Finally, pure sodium borate and 55 per cent sodium borate glasses were investigated, using a sodium amalgam electrode and the small tubes prepared from the glass samples. These last two glasses were not studied at high temperatures because of vaporization of electrodes.

TABLE 1

Conductivity of a sodium borate-boron trioxide mixture

Per cent of $Na_2B_4O_7$ = 5.42

TEMPERATURE	RECIPROCAL OF MEASURED RESISTANCE	SPECIFIC CONDUCTIVITY
degrees C.	*ohm*$^{-1}$	*ohm*$^{-1}$ *cm.*
353.1	8.84×10^{-9}	3.71×10^{-10}
346.0	5.68×10^{-9}	2.39×10^{-10}
344.8	5.05×10^{-9}	2.12×10^{-10}
333.4	2.15×10^{-9}	9.05×10^{-11}
324.2	1.15×10^{-9}	4.84×10^{-11}
310.5	3.42×10^{-10}	1.44×10^{-11}
306.3	3.10×10^{-10}	1.30×10^{-11}
296.0	1.70×10^{-10}	7.14×10^{-12}
280.0	9.50×10^{-11}	3.98×10^{-12}
265.7	2.14×10^{-11}	8.99×10^{-13}
264.3	2.42×10^{-11}	1.01×10^{-13}
260.6	2.08×10^{-11}	8.74×10^{-13}
244.5	1.39×10^{-11}	5.84×10^{-13}
229.0	7.69×10^{-12}	3.23×10^{-13}
211.8	4.30×10^{-12}	1.80×10^{-13}
194.8	2.46×10^{-12}	1.03×10^{-13}

Each of the three pure boron trioxide glasses studied gave conductivity values in good agreement with the others. Plotting log of the specific conductivity (as calculated after evaluation of the cell constant) against reciprocal of the absolute temperature, straight lines over the measured temperature interval were found in every case. The accurate evaluation of the cell constant was rather difficult, and owing to this fact the curves for the three samples were parallel but not identical. The deviations were small and can be attributed without question to the evaluation of the cell constant.

In table 1 the recorded data on one of the three mixtures are given. Smooth curves drawn through the recorded points are shown in figure 1. The curve for pure boron trioxide represents an average of the three samples measured.

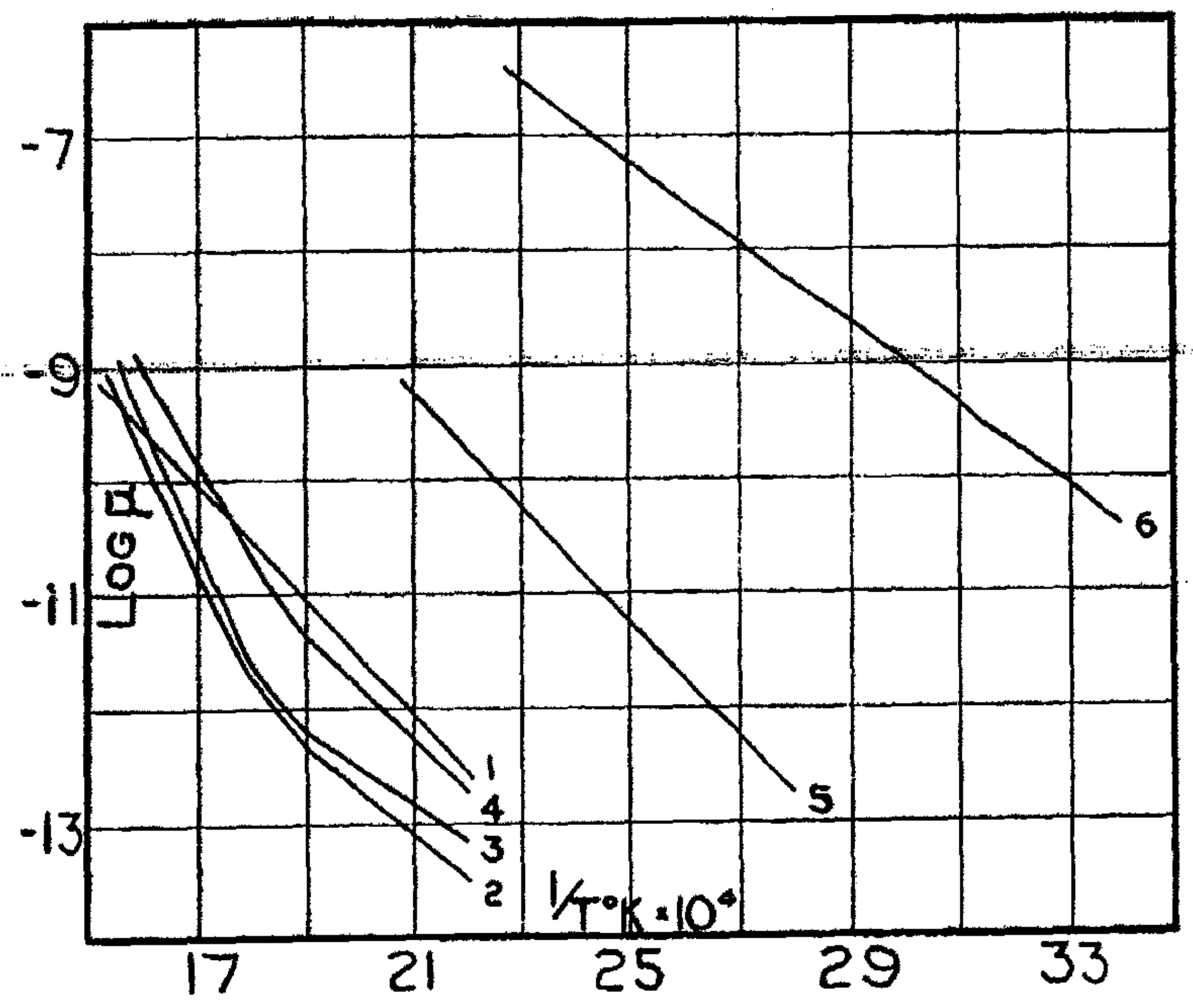

FIG. 1. SPECIFIC CONDUCTIVITY OF BORON TRIOXIDE–SODIUM BORATE GLASSES

1, Pure boron trioxide; 2, mixed glass containing 2.68 per cent sodium borate; 3, mixed glass containing 5.42 per cent sodium borate; 4, mixed glass containing 16.74 per cent sodium borate; 5, mixed glass containing 55 per cent sodium borate; 6, pure sodium borate.

DISCUSSION

The series of curves shown in figure 1 present two marked features: (1) In all cases of mixed glasses which were measured to about 250°C., a decided and rather sharp break was found in the conductivity curve. This break occurred in each of the three glasses measured in this temperature range at a point near the transition region of boron trioxide as determined from other physical data. (2) The addition of a small percentage of sodium borate to boron trioxide lowers the conductivity of the glass in the region of softening. As we go to higher temperatures, however, the mixed glass increases in conductivity more rapidly with temperature than does the pure boron trioxide, and at high temperatures the mixtures are more conductive than the pure oxide.

Neither of the previous investigators of these systems has reported the abrupt changes in the direction of the conductivity curves of the mixed glasses in the transition region. Nevertheless, the data reported by Thomas (6) are in fair agreement with those presented here, especially at the higher temperatures. His values for boron trioxide–sodium borate mixtures show that at low temperatures the specific conductivities would be less than that of pure boron trioxide. Schönborn's investigations on borosilicate glasses (3) show conductivity curves which are of the exact nature of the mixture curves in figure 1.

The significance of the marked change of direction of the mixture curves is to be related to the gradual change in state of a glass in its transition region (2). It is known that a viscous liquid changes to a solid glass in a short temperature interval, and that many physical properties change in this interval with an abruptness that is suggestive of a crystallization process. The conductivity behavior of the mixed glasses seems to be further evidence of this change of state within a narrow temperature interval.

The addition of sodium borate to boron trioxide introduces sodium ions, and thereby evidently brings about ionic conductivity. When a glass conducts a current ionically, a break in the conductivity curve represents a change in the binding forces acting on the conducting ions. This might be expected in every case where the conducting ions are part of the molecules or aggregates composing the glass. If conduction is electronic, or due to foreign ions which are not affected by the glass structure, the transition of a glass to a viscous liquid would not necessarily affect the conductivity. In the case at hand, the presence of sodium ions in the mixtures introduces ionic conductivity, and a change in the direction of the conductivity curves might well be expected in the transition region.

Extrapolating the straight portions of the curves for the mixtures, points are obtained which can be considered as the "transition temperatures" of the glasses. For the three mixtures containing low percentages of borax, these values are 271°C., 279°C., and 276°C., named in the order of increasing sodium borate content. The transition temperature for pure boron trioxide, as chosen from other physical data, is in the neighborhood of 250°C. (6).

The straight unbroken curve for pure boron trioxide suggests that the conduction is not carried on by ions which are part of the glass structure. Many oxides have been found to conduct electronically, and this is probably the nature of the conduction by this substance.

The decrease in conductivity when sodium borate is added to boron trioxide seems to indicate that the addition of ionic conductors disturbs the inherent ability of the boron trioxide to conduct electronically. As the percentage of sodium borate increases, however, the ionic conduction becomes greater, and apparently surpasses that of pure boron trioxide as higher percentages are reached. Even with small amounts of sodium borate (2 to 5 per cent), the ionic conductivity increases so rapidly with temperature that in the neighborhood of 350°C. the conductivity exceeds that of pure boron trioxide. Below the hardening region the curves are approximately parallel.

Although direct current was used in the measurements, polarization effects were not noticeable in the samples containing small percentages of sodium borate. If conduction by pure boron trioxide is electronic, no polarization would be expected in any case.

The glasses containing a high percentage of borax were measured with a sodium amalgam anode which acted as a source of sodium ions and thus prevented polarization. An attempt was made to measure these samples with the Monel cell, but polarization effects were evident. However, measurements were made on the 16.7 per cent sodium borate sample using the amalgam anode, and results were obtained which were in very close agreement with those obtained using the Monel cell. This fact shows that with glasses containing low percentages of sodium borate, polarization is unimportant.

SUMMARY

The electrical conductivities of boron trioxide, sodium borate, and some boron trioxide–sodium borate systems have been measured over a 240° interval with a modified Wheatstone bridge method.

Pure boron trioxide shows a smooth even conductivity curve over the entire measured range, but the mixed glasses gave fairly sharp breaks in the curves in the region of transition of the glasses. These breaks are considered to be associated with the changes in many physical properties in the interval where a viscous liquid changes to a hard glass.

The addition of small percentages of sodium borate to pure boron trioxide causes the conductivity to decrease, but further addition causes a steady increase.

It is our pleasure to express appreciation to Professor George S. Parks and Dr. F. O. Koenig of this department for their help and advice in this work.

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A STUDY OF THE ADSORPTION AT THE BENZENE-SODIUM OLEATE SOLUTION INTERFACE

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Received September 6, 1933

Since Langmuir (11, 12) and Harkins (4) first suggested that an oriented monomolecular layer of adsorbed material existed at the interface of emulsions, considerable experimental work has been done to test the validity of their suggestion. The results obtained are conflicting; some show adsorption equivalent to a monomolecular film, while others give evidence of films of greater thickness.

Griffin (2) attempted to confirm the theory with a study of emulsions of kerosene with solutions of sodium oleate and stearate. He found approximately a monomolecular layer. Van der Meulen and Riemann (17, 18) reported similar results with toluene emulsified with solutions of sodium ricinoleate and sodium oleate. In the latter case phenol was added to the toluene used in preparing the emulsions. Undoubtedly phenol or sodium phenolate was adsorbed at the interface in addition to the sodium oleate. Since the interfacial areas were calculated statistically by these workers from relatively small amounts of material the results are somewhat uncertain.

Studies by McBain and his coworkers (13, 14) on the adsorption of such substances as *p*-toluidine, amyl alcohol, nonylic acid, phenol, etc., at the interface between the aqueous solution and nitrogen gas have repeatedly shown the formation of films more than one molecule thick. With sodium oleate solutions and nitrogen bubbles, Laing, McBain, and Harrison (10) found sufficient adsorption for a dimolecular layer.

Nonaka (20), using a Donnan pipet, studied the adsorption of sodium oleate and palmitate on droplets of toluene and found greater than monomolecular adsorption.

Harkins and Beeman (3) made measurements on emulsions containing a much greater number of droplets than those of Griffin and of van der Meulen and Riemann. Using emulsions of various oleates and octane they failed to find adsorption more than sufficient to form monomolecular films. Harkins and Fischer (5), in examining sodium oleate-paraffin oil emulsions, measured the size of 1000 to 3000 droplets in each emulsion

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studied and computed from these results the distribution of size and the total interfacial area involved. The adsorption found was only sufficient to form a monomolecular film.

All the studies, except those of Nonaka, on the liquid-liquid interface in emulsions of oils with dilute soap solutions have been made by preparing an emulsion in the usual manner and then attempting to estimate the total interfacial area by statistical studies of the size distribution of the droplets. The distribution of the fatty acid between the two phases was permitted to take place during and after emulsification. The measurements on such systems involve approximations which necessitate considerable experimental error. The writers surmise, too, that with the close packing of the oil droplets in such an emulsion, some of the adsorbed material might be squeezed out into the excess of dispersion medium. There is much need for work that is more quantitative and affords more uniform conditions at the interface.

The work presented in this paper is a study of the adsorption of sodium oleate at a water-benzene interface, using droplets of benzene of uniform size. The experimental set-up was similar to that used by McBain and his coworkers (10, 13, 14) in their study of adsorption at a nitrogen gas–aqueous solution interface. This type of apparatus has not been used before with systems having liquid–liquid interfaces. The number and size of the droplets were known, which permitted a quite accurate estimate of the area of the interface. Benzene and sodium oleate solutions were chosen as the two phases, because this system is easily reproducible and has been widely used, thus permitting a greater comparison with the work of other investigators. The experiments differ further from previous work in that the two phases were brought to equilibrium prior to making the adsorption measurements in all but one experiment. In such a system the fatty acid formed by the hydrolysis of the sodium oleate distributes itself between the two phases.

EXPERIMENTAL

Materials

The benzene used was of "C. P. analyzed" quality. It was redistilled and only the middle portion boiling over a one-degree range was used.

Eimer and Amend's "C. P. linolic acid-free" oleic acid, also used by Harkins and Fischer (5), was found to be a very pure product. This acid was used throughout and proved to be very uniform in quality.

The soap was prepared in two ways. That used in the first two experiments was prepared from sodium ethylate and oleic acid in the method developed by Harkins and Beeman (3). Solutions prepared from this soap tended to become turbid, probably owing to the presence of acid soap. In order to avoid this difficulty and any possible contamination from carbonate, the soap solution used in the subsequent experiments was made directly in the 5-liter flask in which the two phases were later allowed to come to equilibrium. The carbon dioxide-free base used in preparing the solution was made (7) by dissolving stick sodium hydroxide, "c. p. from alcohol," in distilled water to form a saturated solution. This was centrifuged and the supernatant liquid used to prepare a concentrated stock solution. It was stored in a paraffined bottle and standardized for later use.

In preparing the soap solution the required amount of the stock sodium hydroxide solution was carefully pipetted into the 5-liter flask. Oleic acid in slightly less amount than that equivalent to the base was then added to the solution and the mixture heated under a reflux condenser until saponification was complete. After cooling, the soap solution was diluted with freshly boiled distilled water until the solution weighed approximately 2250 g. A solution of a weighed quantity of oleic acid in approximately 2500 cc. of benzene was next prepared. The amount of oleic acid was such that if it were added to an equal volume of the soap solution the concentration of the excess sodium hydroxide would still be at least 0.001 *N*.

After the foam which formed on the soap solution during the dilution had disappeared, the benzene solution was added. By running the benzene in with extreme care, the emulsion formed at the interface occupied only a few per cent of the total surface. The weight of the benzene solution added was such that the two phases had an equal volume.

The flask was then placed in a thermostat at 25°C. and the two phases allowed to come to equilibrium. Placing a portion of the oleic acid in the benzene phase greatly shortened the time required to reach equilibrium, since the upward diffusion, into the benzene, of the oleic acid formed by hydrolysis of neutral sodium oleate is very slow. The downward diffusion was hastened by cautiously rotating a bent stirring rod in one phase and then in the other.

Preliminary tests showed that equilibrium was attained in ten days to two weeks as a maximum. This was determined by removing, at intervals, a sample of the benzene phase and determining the concentration of oleic acid. When no further decrease in the acid content could be detected after five days standing, it was assumed that the solutions were at equilibrium.

To provide for rapid attainment of equilibrium in the first two experiments, in which pure solid soap was used to prepare the solutions, a small quantity of oleic acid was added to the benzene and slightly more than an equivalent amount of carbon dioxide-free sodium hydroxide was added to the soap solution.

Although the alkali added in preparing the soap solution used in experiment No. 1 was in excess of the oleic acid added to the benzene phase, the solution never became clear. The solid soap must have contained some free fatty acid or, more probably, some acid soap. Undoubtedly this solution, which showed considerable turbidity, contained a larger amount of colloidal material than would have been found in a clear solution of this dilution.

When it was desired to use the solutions, they were removed from the flask by siphoning into separate bottles. The soap phase was placed in a Pyrex bottle. Care was taken at all times to avoid contamination by carbon dioxide. The bottles were stored in the thermostat and both phases were analyzed as described below.

As a check on the other experiments, experiment No. 7 was made with a soap solution which was not at equilibrium with the benzene phase. The soap solution was prepared to duplicate the materials used in experiment No. 6 as closely as possible. That is, since pure benzene was used, the soap solution was made not only so that it contained very nearly the same normality of sodium as the solution used in experiment No. 6, but also so that it had approximately the oleic acid content which would have resulted if all the oleic acid in a given volume of the benzene used in No. 6 were transferred to an equal volume of the soap solution for No. 6.

Analytical

Owing to the large size of the benzene droplets used in the experiments and the resulting low specific interfacial area (total area in square centimeters / total volume in cubic centimeters of the benzene), the amount of material adsorbed, if a monomolecular layer were formed, was too small to obtain sufficiently accurate results by the volumetric determination of the oleic acid. It was thought that the sodium could be determined with sufficient accuracy by titration. The solutions used in the first two experiments were analyzed in this manner, but satisfactory results were difficult to obtain and in the later experiments the analyses were made entirely by gravimetric methods as described below.

Analysis of the equilibrium benzene solution. Approximately 10 cc. of the benzene solution was weighed into a tared weighing bottle. The benzene was then evaporated under reduced pressure in an oven at 50–55°C. After cooling, the oleic acid was weighed on a Kuhlmann microbalance. Weights were rounded off to five decimal places in grams. Two blanks were run with each set of analyses. A quantity of pure oleic acid approximately equal to that in the sample being analyzed was weighed into tared bottles and 10 cc. of pure benzene were added. The evaporation of the benzene, subsequent cooling, and weighing of the blanks and samples were carried out simultaneously. The weighed samples of oleic acid, used as blanks, usually showed an increase of a few hundredths of a milligram, probably due to a slight oxidation of the acid while in the oven, although little air came into contact with the bottles during evaporation, since the benzene vapor was carried off by the suction. This increase in weight was used as a correction in the determination of the oleic acid in the sample.

From the weight of the sample and the weight of the oleic acid, the concentration in milligrams of oleic per gram of benzene was calculated. The weighings in all analytical work reported in this paper were corrected to weight in vacuo.

Checks on carefully prepared standard solutions of oleic acid in benzene showed that the estimation of the acid by microgravimetric means was far more accurate than by titration with standard aqueous or alcoholic sodium hydroxide. In fact, considerable time was lost in unsuccessful attempts to titrate the oleic acid according to the methods used by previous investigators.

Analysis of equilibrium soap solutions. For this analysis special tubes of Pyrex glass were prepared by sealing a piece of tubing 1 cm. in diameter and 8 cm. in length to a test tube 2 cm. in diameter and 22 cm. in length. A sample of the equilibrium soap solution was placed in the tared tube and weighed. An excess of dilute sulfuric acid solution was then added, weighed, and finally 10 to 12 cc. of pure benzene saturated with water was added and weighed. The tube was sealed off and placed in a horizontal position in a slow rocker. After several hours the oleic acid was completely extracted by the benzene, both phases becoming clear. The neck of the tube was next cut off and a sample of the benzene solution was pipetted into a tared bottle and weighed. The benzene was evaporated as described above and the oleic acid weighed on the microbalance. Weighing bottles containing the proper weight of oleic acid were used as blanks. This procedure afforded the necessary data for the calculation of the concentration of oleic acid per gram of the soap solution.

This method was checked by analysis of a prepared standard soap solution 0.01522 N_w (weight normality), with the following results. Theoretical: 4.298 mg. oleic acid per gram of soap solution. Found: 4.295 mg. per gram.

In the first two experiments standard acid was added to the soap in the extraction tubes and the sodium was determined by titrating the excess acid with standard alkali. Difficulties in obtaining check results led to the use of the following method. A sample of the aqueous phase remaining in the extraction tube after the removal of the benzene was weighed into a tared platinum crucible. The water was evaporated in the oven by the same method as described for the benzene. The sodium sulfate was ignited in a muffle to constant weight and weighed to five decimal places in grams on the Kuhlmann balance.

Apparatus and procedure for carrying out an experiment. The apparatus was a modified form of the one used by Laing, McBain, and Harrison (10) and is shown in figure 1. A and B are reservoirs for the equilibrium benzene solution. This arrangement was used in order to maintain a constant head of solution in B. Tube M connected bulb B to a gas washing bottle used to saturate the incoming air with benzene vapor. Stopcock C permitted regulation of the flow of benzene solution through the tip E. This tip was made by a careful thickening of a length of small Pyrex tubing and drawing it out to the proper diameter. The orifice was circular and the end was ground smooth. Preliminary work showed that the tip should be of a size to produce a benzene droplet approximately 2 mm. in diameter.

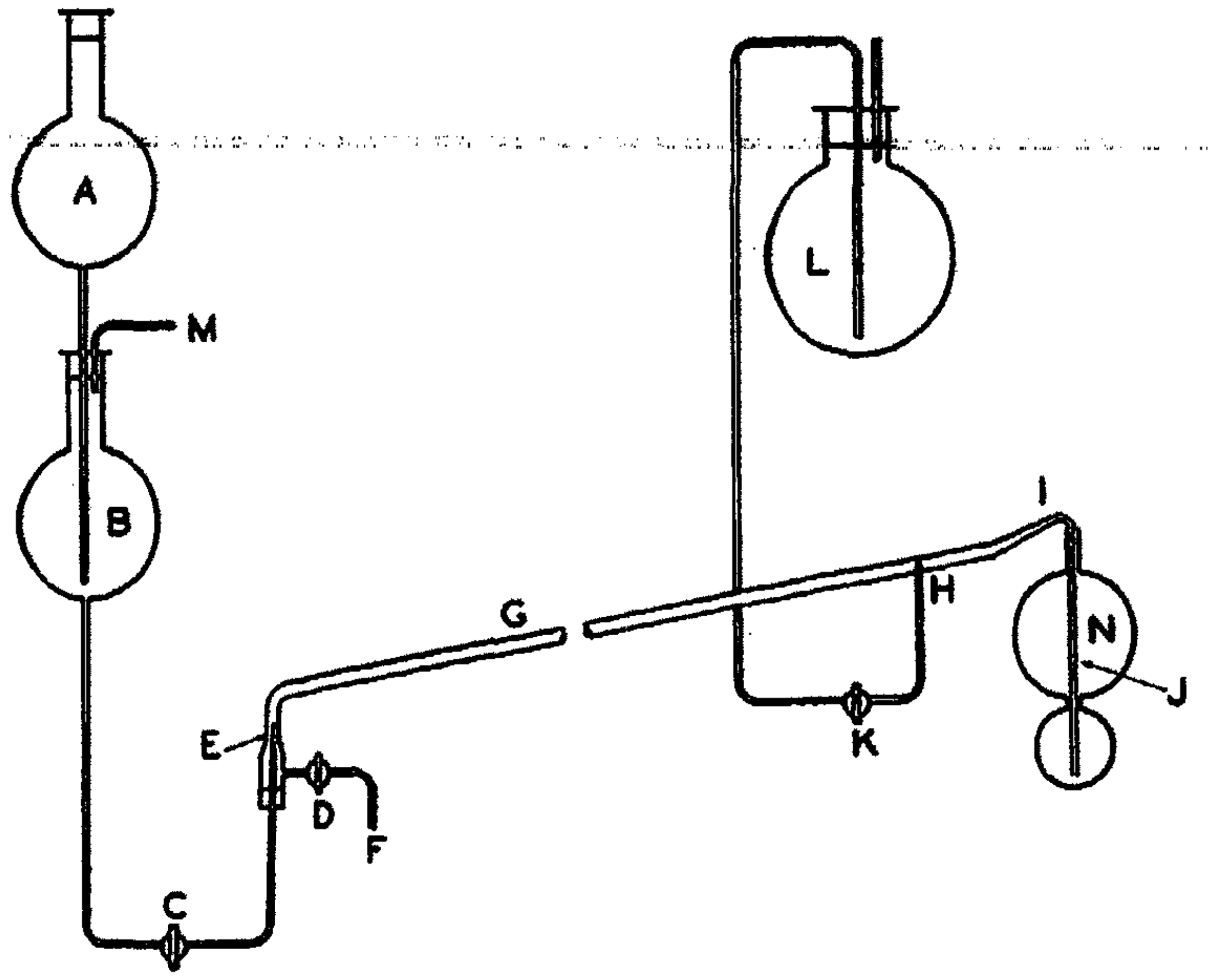

FIG. 1. ADSORPTION APPARATUS

With larger spheres the volume of benzene needed to form a sufficient number of droplets would be too great. Smaller droplets were very difficult to count accurately when the benzene flow was rapid enough to complete the run in a reasonable time.

Benzene droplets of this size did not appear to be deformed in any way during the passage through the adsorption tube and over the bend I, and in our calculations we have considered them to be perfect spheres.

L is the reservoir for the equilibrium soap solution. The tube H, through which the soap solution entered the adsorption tube G, projects about two-thirds of the way across the tube G, since preliminary work showed this was necessary in order to prevent the solution simply running down the bottom wall of G and out the tube F without appreciably mixing with the solution in the tube. Tube G was approximately 100 cm. long, with an inside bore of 1 cm., and a volume of about 75 cc.

This tube made an angle of about 10° with the horizontal except for the last three centimeters before the bend at I. Here the slope was slightly steeper, and the tube was narrowed down until at the top of the bend the diameter was between 2 and 2.5 mm. The change in slope was small, as it was found that when the tube was steeper than 15° to 20° the benzene droplets jammed together and lost their spherical shape. The slight change in slope at the end of the tube served to separate any groups that formed as the droplets travelled up the tube.

The actual time each droplet was in the tube varied in the different runs from seventy seconds to nearly two minutes. This was much longer than the time the nitrogen bubbles used by Laing, McBain, and Harrison (10) and by Harkins and Gans (6) remained in the adsorption tube.

The collection flasks used were made by sealing a 100-cc. round bottom flask to the bottom of a similar 300-cc. flask (N, figure 1). Then the neck of the large flask was drawn out and a piece of tubing a few centimeters long and 1 cm. in diameter was sealed to it.

Before each experiment the entire apparatus was carefully cleaned with potassium dichromate–sulfuric acid cleaning solution, thoroughly rinsed with distilled water, and dried.

In making a run the apparatus was filled and the benzene flow adjusted so that about three droplets were formed per second. Then the stopcock D was regulated to allow between 100 and 200 cc. of soap solution to flow out during the run. Since the size of the drops from tube D varied with the concentration of the soap, and since it was found very unsatisfactory to make other than the small adjustments necessary to keep the run going smoothly after the start of the experiment, the amount of soap used as back current fluctuated considerably over the range 100 to 200 cc. per run. This was found sufficient, however, to prevent changes in concentration of the soap in the adsorption tube.

Finally, the flow of soap solution into the apparatus was so regulated that the droplets of benzene did not pack as they passed over the bend at I, and yet the excess of soap solution accompanying them was kept as low as possible.

Since the benzene droplets could not be carried up a steep tube and thereby drained of the excess of soap solution, as was done by Laing, McBain, and Harrison (10) with nitrogen bubbles, the solution in the receiving flask was only slightly more concentrated than that in the adsorption tube. This factor combined with the low specific interfacial area makes the determination of the actual adsorption one requiring very carefully executed technique.

When all the adjustments were properly made the weighed collection flask was saturated with benzene vapor, pushed up on the tube J, and lightly stoppered to prevent evaporation of benzene vapor. The time of placing the flask in position was recorded and the length of the run was accurately timed. Every five minutes during the course of the run the speed of formation of droplets was measured. This was done by noting, with the aid of a stopwatch, the time required for fifty droplets to pass a given point on the tube. From these readings, and the time elapsed during the run, the total number of droplets was computed. From the weight and density of the benzene collected the volume and the surface of the droplets were calculated.

The temperature of the room was held very constant during the course of a run. At rare intervals and then only for a few minutes at a time did the temperature vary more than ± 0.5°C. from 25°C.

Except for the first two experiments, duplicate runs were made consecutively with no break in time. In the first two experiments only one run was made in a day and the check run was made the following day.

After completion of a run the analytical procedure described above was immediately carried out. The data of the experiments are given in table 1.

Determination of weights of materials used and calculations of results. Previous to placing flask N in position its weight (W_E) was carefully determined to ± 2 mg. At the completion of the run the weight (W_T) of the flask plus the solutions was found. Then a quantity of sulfuric acid was added in excess of that necessary to react with the sodium present. The flask was again weighed (W_A) and sealed.

By shaking the flask from time to time the oleic acid was extracted from the soap solution by the benzene. When extraction was complete the flask was opened and the greater portion of the benzene phase transferred by a siphon to a glass-stoppered bottle. The residue of the benzene was removed with a pipet and the upper bulb rinsed with petroleum ether. The last traces of the ether were driven out with a gentle stream of air, which was saturated with water vapor in order to prevent evaporation of the aqueous phase. After the removal of the benzene, the weight (W_U) of the flask and aqueous solution was determined.

The benzene layer was analyzed for oleic acid and the aqueous phase for sodium in the manner described above.

From these data the weights of the solutions used were found as follows: $W_T - W_E = W_R$, total weight of solutions used in the run. $W_A - W_W = W_{BO}$, weight of benzene solution plus oleic acid from soap solution. $W_R - W_{BO} = W_S$, weight of soap solution used minus its oleic acid. The weight of the oleic acid (W_O) removed from the soap solution by extraction can be found from the analysis of equilibrium soap and W_S. Then $W_S + W_O = W_{SU}$, weight of soap solution used. $W_{BO} - W_O = W_B$, weight of benzene solution used in forming droplets.

TABLE 1

Adsorption at the benzene-sodium oleate solution interface

	EXPERIMENT NO.											
	I		II		IV		VI		VII		VIII	
	A	B	B	C	A	B	C	D	A	B	A	B
Oleic acid concentration, pre-run*	8.12	8.12	22.63	22.63	80.28	80.28	47.49	47.49	50.74	50.74	91.08	91.08
Sodium concentration, pre-run†	11.13	11.13	25.59	25.59	83.27	83.27	51.65	51.65	52.37	52.37	99.50	99.50
Oleic acid concentration, benzene‡	4.95	4.95	2.46	2.46	16.97	16.97	3.61	3.61	0.00	0.00	1.34	1.34
Excess sodium concentration§	3.01	3.01	2.96	2.96	2.99	2.99	2.16	2.16	1.63	1.63	8.42	8.42
Sodium concentration after run¶	11.23	11.22	25.80	25.80	83.78	83.85	51.88	51.80	52.57	52.79	100.25	100.52
Aqueous phase used (grams)	96.9	113.8	98.4	92.6	67.3	62.4	65.44	74.04	66.07	65.90	56.05	53.65
Benzene solution used (grams)	293.7	278.6	264.5	234.1	176.0	181.2	221.3	239.4	253.0	252.6	184.9	191.7
Total number of droplets × 10^{-3}	60.50	59.80	61.50	64.40	60.00	61.40	48.30	49.00	41.10	41.50	50.30	50.00
Rate droplets per second**	2.71	3.06	3.10	3.12	4.17	4.27	3.35	3.40	3.42	3.46	3.50	3.47
Mean diameter droplets (mm.)	2.20	2.17	2.11	2.00	1.86	1.86	2.16	2.20	2.38	2.37	2.01	2.04
Oleic acid gain (mg.)	59.9	53.0	26.4	24.8	41.8	43.4	47.9	50.9	40.3	44.3	40.4	47.8
Sodium gain (equivalents) × 10^6	9.694	10.24	20.3	19.5	35.0	36.0	13.74	8.88	13.2	27.6	42.0	54.7
"Layers" from oleic acid††	28.8	26.5	13.6	13.6	28.4	28.7	30.0	30.1	24.1	26.7	28.4	32.6
"Layers" from sodium‡‡	1.3	1.4	2.9	3.0	6.7	6.7	2.5	1.5	2.3	4.7	8.5	10.5
Specific interfacial area§§	27.2	27.6	28.4	30.0	31.4	32.2	27.8	27.3	25.2	25.3	29.5	29.4
Total time of run (minutes)	365	325	330	340	240	240	240	240	200	200	240	240

* Normality of equilibrium soap solution times 10^3. All concentrations for aqueous phases are given in weight normality.

† N_w aqueous phase times 10^3.

‡ Equilibrium benzene solution normality times 10^3. Volume normality calculated from weight analysis and specific gravity.

§ Sodium excess in equilibrium soap solution, $N_w \times 10^3$.

¶ $N_w \times 10^3$.

** Mean rate of formation of droplets during the run.

†† Number of monomolecular films equivalent to oleic acid gain.

‡‡ Number of monomolecular films equivalent to sodium gain.

§§ Total surface of droplets in square centimeters divided by total volume of benzene used in cubic centimeters.

Letting C represent the concentration (milligrams of oleic acid per gram of solution) of the solutions whose subscripts are used, we find the total gain in oleic acid as follows: $W_{BO}C_{BO} - W_BC_B - W_SC_S$ = mg. of oleic acid total gain.

The computation of the sodium gain was somewhat simpler. The difference between the normality of the sodium concentration in the equilibrium soap solution and the normality found for the soap solution collected gave the change in normality. This value multiplied by the number of cubic centimeters of soap solution carried over during the run and divided by 1000 gave the gain in equivalents of sodium.

The formulas for comparing the results obtained in these experiments with the gains which would have been required for monomolecular layers were derived as follows: Let M equal the weight in grams of benzene solution used, N the total number of benzene droplets formed, and G the milligrams of oleic acid gained during the run. The density of the benzene solutions used was equal to 0.873. The surface of a sphere is equal to $12.57 \frac{(v)^{\frac{2}{3}}}{(4.189)}$, where v is the volume. Other constants used are: 6.06×10^{23}, Avogadro's number; 282.3, the equivalent weight of oleic acid; and 20.6 Å.,[2] the mean cross-section (1) of a fatty acid molecule.

From these values the following formula was derived:

$$\text{“Layer”} = \frac{(20.6)[(4.189)(0.873)]^{2/3}\,(6.06)\,10^{7}G}{(12.57)(1000)(282.3)(M^{2}N)^{1/3}}$$

This reduces to:

$$\text{“Layers”} = \frac{(835.4)G}{(M^{2}N)^{1/3}}$$

This formula was modified to use with sodium gains, since by the method of calculation the gains were in equivalents. Using G in equivalents and multiplying the above formula by 1000 and 282.3, it becomes:

$$\text{“Layers”} = \frac{2.358 \times 10^{8}G}{(M^{2}N)^{1/3}}$$

It should be understood that the calculation of gain in "layers" is purely for the purpose of comparison with the amount necessary for the production of a monomolecular layer, and does not mean that the authors conceive of any such phenomenon as twenty or thirty layers of films at the interface.

RESULTS AND DISCUSSION

The results obtained were rather striking. In no case did the adsorption, as calculated from the gain in oleic acid, approach a monomolecular film.

In fact, with the one exception of experiment No. 2, the gain was more than twenty times that sufficient to form a film one molecule deep.

The adsorption calculated from the gain in sodium was much less. Though we found no adsorption so small as a monomolecular layer, three runs gave values less than sufficient for a dimolecular film, and in only four runs were the gains greater than five times that for a single layer of molecules.

A consideration of the experimental errors in analytical results and in counting the droplets showed that should all possible errors be cumulative they would not exceed 5 per cent of the amount of adsorption. It should be pointed out that there are several factors which, while probably negligible, would tend to make our results low rather than high. Though there was very slight drainage of the droplets it is possible that some of the adsorbed material could be brushed away from the surface in the adsorption tube. Another possibility is that oleic acid might be adsorbed from the benzene to the interface. Such an adsorption would not be shown by our procedure.

It is somewhat difficult to find a completely satisfactory explanation of the cause for this great difference in the amount of adsorption as measured by the gains found in the two constituents of the soap solution. A careful consideration of the results of other workers on the problem of adsorption of soap at the oil-solution interface, as well as of the studies made on the structure of the particles of sodium oleate in solution, brings out considerable suggestive material.

Laing (9) and Laing, McBain, and Harrison (10) have demonstrated the adsorption of acid soap at a nitrogen-sodium oleate solution interface. They reported a mean ratio of oleic acid to sodium of 1.70, which would account for an acid soap of the composition $NaOl \cdot 0.77\ HOl$.

Nickerson and Serex (19) studied the conductance of sodium oleate solutions in contact with benzene with results from which they conclude: "More acid sodium oleate is adsorbed at the oil-solution interface than at the vapor-solution interface," and "the rôle of acid sodium oleate has been much underrated."

Adsorption of the simple acid soap molecules, while undoubtedly a factor in the experiments we have made, would hardly account for the large ratio found between the gain in oleic acid and sodium in some of the runs.

From the results of experiments on the adsorption of sodium oleate and sodium palmitate at benzene and toluene interfaces, Nonaka (20) reached the conclusion that the adsorption of both soaps was of monomicellar rather than monomolecular order. He conceives of the micelle as consisting of the combination of the fatty acid micelle and neutral soap micelle in a tangled state. Later cataphoretic studies, in which Nonaka (21) used the same materials, led him to believe that the surface active material of the soap solutions must be the ionic micelle in all cases.

Thiessen and Spychalski (22) and Thiessen and Triibel (23) have made careful examination of the structure of sodium oleate in solutions by means of x-ray and double refraction studies, and conclude that the same micelles exist in solution as in gels (see also McBain and McBain (16)). These micelles Thiessen finds are rod-like, with the long chain of the fatty acid lying at right angles to the long axis of the rod. Two of the long faces of the micelles are made up of the carboxyl end of the soap. Thus in a neutral soap these faces would present a solid array of sodium atoms. If the micelle is not neutral some of the sodium atoms would be replaced by hydrogen. If micelles of this form should be adsorbed, the oleic acid gain would be much greater than that of the sodium.

Most of the work on the presence of micelles in soap solutions has been done at higher temperatures or at higher concentrations than we have used. However, in their determination of the micelle content of solutions of sodium oleate by means of ultrafiltration, McBain and Jenkins (15) worked with more dilute solutions and at 18°C. They could find no micelles in a 0.01 *N* solution, but using a 0.144 *N* solution the filtrate was only 0.001 *N*, indicating that nearly all of the material was of a colloidal nature. In discussing this work McBain says, "The 0.01 *N* solutions were filtered immediately after being prepared. It is possible that the colloidal acid soap formed by hydrolysis had not yet agglomerated sufficiently to be held back."

Later work by Laing (8, 9) in McBain's laboratory has afforded convincing evidence of the presence of ionic micelles in sodium oleate solution as dilute as 0.01 *N*.

The work alluded to indicates the probable presence of large molecular aggregates in sodium oleate solutions. It is not inconsistent to expect that such aggregates should be adsorbed at the benzene–solution interface. Such adsorption is in accord with the findings reported herein.

SUMMARY

1. An analytical method has been devised which is more accurate than the customary method of determining oleic acid.

2. A study has been made of the adsorption of sodium oleate at the benzene–sodium oleate solution interface. The adsorption found, as calculated from the gain in oleic acid, was, with the exception of experiment No. 2, equivalent to that necessary to form from twenty to thirty monomolecular films. The adsorption, as calculated from the sodium gain, varied from that nearly small enough for a monomolecular layer to that sufficient for ten such films.

3. Experiments have been made using solutions at equilibrium as well as non-equilibrium solutions. Similar results were found in both cases.

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NEW BOOKS

Elementary Quantitative Analysis. Theory and Practice. By Hobart H. Willard and N. Howell Furman. 14 x 22 cm.; viii + 406 pp. New York City; D. Van Nostrand Co., Inc., 1933. Price: $3.25.

This book by two of America's leading contributors to analytical chemistry presents more than enough theoretical and practical material for two semesters of work. Thus teachers are enabled to choose their determinations judiciously according to the samples available for analysis and the interests and aptitudes of their students. Although there has been a tendency in recent years to teach analytical chemistry mainly for the purpose of illustrating certain principles of physical chemistry, this text not only gives a thorough presentation of theoretical derivations and interpretations, but also describes an unusually large number of analytical determinations with that patient attention to detail which is essential for the successful guidance of beginning students.

The introduction of many new methods presents analysis as a living, growing branch of chemistry. The theory of adsorption indicators is carefully explained, and the Fajans method for chlorine in a soluble chloride is described in adequate detail. Although some recent texts make little or no mention of internal indicators for use with standard solutions of oxidizing agents, the authors have discussed these carefully and have described the use of sodium diphenylaminesulfonate in the bichromate method for iron. There is also an excellent section on ceriometry, which is based largely on the authors' own researches.

An interesting innovation in gravimetric analysis is the addition of urea to a solution from which calcium is to be precipitated with ammonium oxalate. Because of the hydrolysis of the urea into carbon dioxide and ammonia and the consequent slow neutralization of the slightly acidified solution, the calcium oxalate comes down in a very coarse form.

The solutions of many typical problems and the thought-provoking questions will be a great aid to both student and instructor. On pp. 272-3 two methods are given for calculating the results of indirect analyses. The second of these is by far the better. Because of the large errors involved in indirect analyses, very little space has been devoted to calculations of this type. The detailed discussions of the interfering substances and errors involved in each method and the various applications of each procedure are especially valuable.

Because of the wide scope of the book and its frequent references to the original literature, many thoughtful students will wish to keep it for their permanent libraries. Experienced analysts, also, will find in it many helpful suggestions.

Mary Elvira Weeks.

Physical Constants, Selected for Students. By W. H. J. Childs. 17 x 10 cm.; viii + 77 pp. London: Methuen & Co., 1934. Price: 2s. 6d.

The dimensions of this small book, one of the publisher's series of monographs on physical subjects, comply with the intention of the author to present useful lists and tables in a form compact enough to go easily into the pocket.

The data chosen, under the headings General, Heat, Light, Magnetism and Electricity, and Sound, will be found useful to the physicist. A somewhat different selection of material is needed to be of most use for the physical chemist, e.g., the replacement of astronomical and geodetical data by a more extended list of melting and boiling points and more information on definite chemical compounds. Units are defined, but only one calorie is mentioned. Conversion factors are few; there is none for electrical energy to heat. The data given for the surface tension of salt solutions imply that the latter is proportional to concentration.

At the end a list of general constants is given and mathematical tables which include four figure logarithms.

A pleasing feature of the book is the inclusion of seven nomographs which are practicable even within the small compass which the size of the pages allows.

W. H. Patterson.

Physico-chemical Methods. By J. Reilly and W. N. Rae. Second edition, revised. New York: D. Van Nostrand Co.

In the comparatively brief time since the first edition appeared, this book has become widely known and generally accepted as a reference book of physico-chemical methods. The second edition has been enlarged by the addition of new subject matter (twenty new chapters), and to some extent by the revision of the entire book.

The general revision still leaves something to be desired, since in a number of instances no reference is made to recent improvements of standard methods. For example, the use of butyl phthalate in condensation pumps is not mentioned. No reference is made to circulating pumps of the all-glass electromagnetic type. The extremely practical sensitive quartz spiral manometer of Bodenstein and Dux is not mentioned, although several other manometric devices of rather doubtful utility are described in detail. The Dennis melting point apparatus is not referred to. It is unfortunate that the chapter on photometry was written before the copper—cupric oxide (photronic) type of photoelectric cell came into general use.

The chapter on rates of reaction is not, in the opinion of the reviewer, up to the standard set by the rest of the book. This chapter consists of a brief discussion of the elementary theory of rates of reaction followed by detailed descriptions of seven experiments. The chapter would be much more useful if the space were devoted to a critical survey of methods available for measuring rates of reaction.

There can be no doubt, that, in spite of minor weaknesses, this book is an improvement on the excellent first edition. It is a highly practical book and will undoubtedly prove a time saver to many research students and investigators.

Robert S. Livingston.

The Kinetics of Reactions in Solution. By E. A. Moelwyn-Hughes. Oxford: Oxford Press, 1933.

In this book the author attempts the difficult task of summarizing the more important data on the kinetics of chemical reactions in liquid systems and of coördinating this data in terms of the results of statistical mechanical analysis. Special emphasis is laid upon the experimental results which are in agreement with the predictions of the simple theory; and various explanations are advanced to demonstrate that the cases which are apparently not in agreement with the simple theory are not incompatible with it.

As is probably unavoidable in a work of this sort, the chapters are not of equal value. Three of the most original and valuable chapters are those dealing with the comparison of the kinetics of reactions in gaseous phase and in solution, with bimolecular reactions, and with unimolecular reactions. The chapter on equilibria seems unnecessarily involved, possibly because the activity concept is not introduced earlier in the chapter. The discussion of complex reactions, in the chapter on ionic reactions, is somewhat disappointing. The discussion of enzyme reactions, in the chapter on heterogeneous reactions, while brief, is both interesting and stimulating. The bibliographies given are extensive enough to be useful, but in many cases are far from complete. To the reviewer there appears to be some bias in favor of articles which have appeared in English journals.

No student of physical chemistry who is interested in any phase of the kinetics of chemical reactions in liquid systems can afford to ignore this book. It should also prove very useful to organic chemists, biochemists, and others who utilize reaction velocity measurements in the study of their own problems.

Robert S. Livingston.

The Kinetics of Chemical Change in Gaseous Systems. By C. N. Hinshelwood. Third edition. 390 pp. Oxford Press, 1933. Price: $5.00.

Since the appearance of the first edition of this book in 1926 (second in 1929) notable advances have been made in the field of chemical kinetics of gases, to which the author has been an outstanding contributor. The present treatise is not only modern and authoritative but presented with unusual clarity.

One new chapter has been added, "Homogeneous Catalysis of Gaseous Reactions," which affords a very natural transition to some considerations of reactions in solution. Much new material has been added throughout which brings the work abreast of the present status of gas kinetics. The work will continue to be indispensable to all those interested in this field.

S. C. Lind.

Elementare Einführung in die Quantenmechanik. By K. K. Darrow. Translated from the English by E. Rabinowitsch. 22 x 15 cm.: 123 pp. Leipzig: S. Hirzel, 1933. Price: 6 RM.

Dr. Darrow, of the Bell Telephone Company's laboratories, is already well-known as a writer of unusual clarity and grace of style on many subjects of modern physics. In particular his "Electrical Phenomena in Gases" stands out as one of the very few comprehensive treatises on this subject. The present book follows naturally on the author's "Elementare Einführung in die Wellenmechanik" and forms the third volume in a series of books on new problems of physics and chemistry. The book is divided into two main parts, the first of which discusses the wave and corpuscular nature of matter and radiation, the wave equation, and the uncertainty principle of Heisenberg. These sections particularly are to be commended for their lucidity. Part II deals with the main subject matter of the book, quantum mechanics and the emission and absorption of light by atoms. The elementary principles of matrix algebra are considered and the author goes on to discuss the calculation of *eigen*-values by the matrix method and to demonstrate the connection between the wave mechanical and matrix treatment of atomic problems. As the title indicates, the whole is set out with the minimum of mathematical elaboration consistent with the thesis. The book should form an admirable introduction to one of the fundamental aspects of modern physics. Although originally written in English it has not, so far, been published in that language. All students of physics and chemistry who can read simple straightforward German are certain to derive benefit from this little book.

J. T. Randall.

Ueber heterogene Gleichgewichte chemischer Stoffe in Wissenschaft, Natur und Technik. By Ernst Jänecke. 25 x 16 cm.; 31 pp. Stuttgart: Ferdinand Enke, 1934. Price: 2.70 RM.

In this brochure, published in the well-known "Ahrens'sche Sammlung," now edited by Professor Grossmann, one of the foremost workers in the domain of heterogeneous equilibria gives a rapid survey of the principles of the phase rule as applied to systems of 1 to 5 components, with special reference to systems which are of importance in nature and in industry. The exposition, although necessarily brief, is clear and is made all the more easy to follow by the excellent diagrams which accompany the text. Advanced students will find this an excellent summary of some of the more important applications of the phase rule.

ALEX. FINDLAY.

Physica (Volume I, No. 1, December, 1933). 24 x 16 cm.; 96 pp. The Hague: Martinus Nijhoff. To be published in monthly parts, at a price not exceeding 25 guilders for the volume of 960 pages each year.

This new periodical takes over part of the title of *Physica, Nederlandsch Tijdschrift voor Natuurkunde*, which has been appearing since 1921. The *Tijdschrift* is to continue publication in Dutch, but the new *Physica* will contain, in English, French, or German, all original contributions to physics of the Dutch centers of research, and will serve also as a continuation of the *Archives Néerlandaises des Sciences Exactes et Naturelles.*

The introduction of a new periodical will be received with, at best, mixed feelings by all institutions working under strictly limited library allocations. An earlier circular from The Hague points out, however, that the contributions of Dutch physicists will no longer appear in the accustomed foreign, mainly German, periodicals; as the latter are generally sold by weight, it is argued that the advent of *Physica* will therefore involve no net increase in world expenditure on periodicals. There is incontrovertible logic in this, but the average illogical laboratory dweller will not easily be convinced, and it is only too likely that the members of his library committee will share his doubts.

The inevitable protest against any new periodical, *as such*, being discharged, it remains to review this latest example on its merits. The first number contains eight papers, covering a wide range of topics: adiabatic cooling of paramagnetic salts in magnetic fields (de Haas, Wiersma, and Kramers); concentration of Na atoms and Na^+ ions in the sodium low-voltage arc (Druyvesteyn); emission of light in gas discharges (de Groot); design of quartz-fluorite achromat (van Heel); dipole measurements with very small quantities of material (Henriquez); relative abundance of Li^7 and Li^6 isotopes (Ornstein, Vreeswijk, and Wolfsohn); photographic sum rule (van Kreveld); and Tchebycheff polynomials (van der Pol and Weyers).

Detailed discussion of these would be out of place here, but it may be said at once that the new periodical will rank as an important physical journal, with an appeal to a proportion of physical chemists as well as to all physicists. It has a distinguished editorial board, representative of the seven great research institutions of the Netherlands, on which it will rely for its articles. In view of the quantity and quality of the work now issuing in an unbroken stream from these sources, *Physica* seems assured of success from the outset.

H. R. ROBINSON.

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THE JOURNAL OF PHYSICAL CHEMISTRY

Contents

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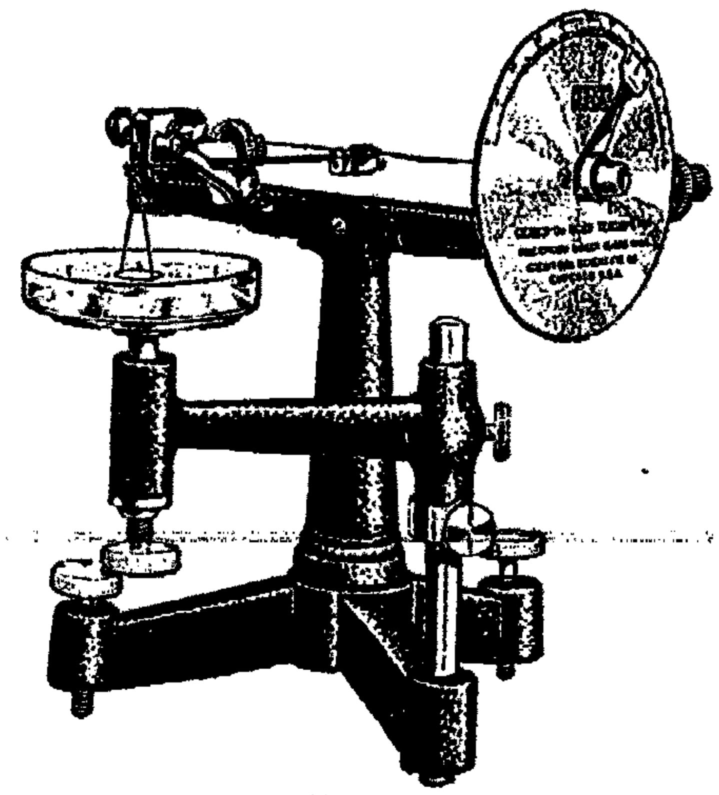

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[1] Harkins and Jordan, J. Amer. Chem. Soc., 52, 1751 (1930).
[2] Freud and Freud, J. Amer. Chem. Soc., 52, 1772 (1930).

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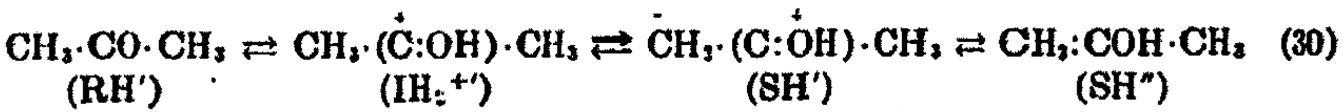
ERRATA

VOLUME 38, NUMBER 5

Owing to the fact that Dr. Pedersen did not read proof for his three papers appearing in this issue, the following changes should be made:

Page 560. For (14) in the 27th line, read (11).
Page 561. For ϕ in the 8th line, read φ.
Page 565. For $\beta = \frac{0.4343K}{\varphi(a + K^2)}$ read $\beta = \frac{0.4343K}{\varphi(a + K)^2}$
Page 566. For 0.5005 in the 4th line of the first column of table 4, read 0.05005.
Page 567. For 32.7 in the last column of table 8, read 23.7.
For "acid" in the heading of table 8, read "and."
Page 584. Formula 9 should read $\frac{k_A}{p} = G\left(\frac{q}{p} K_A\right)^\alpha$
Page 585. For $\frac{g_0}{q_-}$ in formula 14, read $\frac{g_0}{g_-}$.
For $\frac{\pi_{BH^+,R^-}}{\pi_{BH,R}}$ in the formula following formula 14, read $\frac{\pi_{BH^+,R^-}}{\pi_{BH,R^-}}$
Page 589. For "body" in the 13th line, read "both."
Page 593. For $\Sigma\pi_{A,I^-}(A)$ in the middle one of the three formulas following formula 26, read $\Sigma\pi'_{A,I^-}(A)$.
For π'_{A,I^-} in the 24th line, read π''_{A,I^-}.
Page 596. The formula in the middle of the page should read



$$\underset{(\mathrm{RH}')}{\mathrm{CH_3 \cdot CO \cdot CH_3}} \rightleftarrows \underset{(\mathrm{IH}_2^{+\prime})}{\mathrm{CH_3 \cdot (\overset{+}{C}:OH) \cdot CH_3}} \rightleftarrows \underset{(\mathrm{SH}')}{\mathrm{\overset{-}{C}H_2 \cdot (C:\overset{+}{O}H) \cdot CH_3}} \rightleftarrows \underset{(\mathrm{SH}'')}{\mathrm{CH_2:COH \cdot CH_3}} \quad (30)$$

Page 598. For $\mathrm{O:C \cdot CH_2} \rightleftarrows$ in formula 33, read $\mathrm{O:C \cdot CH_2} \rightleftarrows$.
Page 600. For **1927** in reference 22, read **1926**.
Page 602. The fourth formula should read

$$(\mathrm{H^+}) = (\mathrm{H^+})_0 + \kappa \frac{x}{4}$$

Page 609. For k_{HB} just below the heading of table 5, read K_{HB}.
Page 618. For $G^* \times 10$ in the heading of the last column of table 14, read $G^* \times 10^2$.

A THIRD ORDER IONIC REACTION WITHOUT APPRECIABLE SALT EFFECT

HERMAN A. LIEBHAFSKY AND ALI MOHAMMAD

Department of Chemistry, University of California, Berkeley, California

Received November 24, 1933

A kinetic investigation (7), under the simplest experimental conditions, of the reaction

$$H_2O_2 + 3I^- + 2H^+ = 2H_2O + I_3^- \qquad (1)$$

has confirmed the rate law

$$d(I_3^-)/dt = k_1^0\,(H_2O_2)\,(I^-) + k_1(H_2O_2)\,(I^-)\,(H^+) \qquad (2)^1$$

previously discovered, and usually explained by assuming that the two rate-determining steps

$$H_2O_2 + I^- \xrightarrow{k_1^0} H_2O + IO^- \qquad (3)$$

$$H_2O_2 + I^- + H^+ \xrightarrow{k_1} H_2O + HIO \qquad (4)$$

proceed simultaneously and independently. Within the ionic strength range investigated (μ_c = 0.05 to 0.5), reaction 4 was concluded to be without appreciable salt effect, a conclusion so unusual for reactions involving more than one ion that another investigation was undertaken to test it; confirmation thereof is, we believe, furnished by the results that are to be presented here.

If (H_2O_2) is so small that (H^+) and (I^-) remain sensibly unchanged as reaction 1 proceeds, equation 2 may be written

$$d(I_3^-)/dt = k'(H_2O_2) = \{k_1^0(I^-) + k_1(I^-)\,(H^+)\}\,(H_2O_2) \qquad (2a)$$

and k' may be evaluated as though it were the specific rate of a first-order reaction. Values obtained by measuring the rate at which I_3^- appears in reaction mixtures differing initially only in acid concentration may be plotted against (H^+), as in figure 1; when divided by (I^-), the slope of the resulting straight line gives directly the value of k_1, and the intercept similarly yields that of k_1^0. From one such series of reaction mixtures to

---

[1] At 25°C., k_1^0 = 0.69 at low ionic strengths, and k_1 = 10.5. ( ) will be used to denote "concentration of" in moles per liter. → will be restricted to reactions that may be rate-determining. Throughout, the minute constitutes unit time.

another, the ionic strength may be altered by the addition of some salt, e.g., sodium perchlorate; k_1^0 and k_1 may thus be obtained at different ionic strengths. Such measurements have been made; the results thereof are given in tables 1 and 2, and plotted in figures 1 and 2.

For sodium or barium perchlorate in moderate amount as added salt, these data show that the first term in equation 2, involving k_1^0, varies linearly with the ionic strength, while the second, involving k_1, is independent of it.[3] (We shall not at present be concerned with the curvature apparent in figure 2 at the highest ionic strengths.) Granting the plausible kinetic interpretation that has been advanced for the rate law, equation 2, we must conclude that, although reaction 3 shows a "linear" salt effect

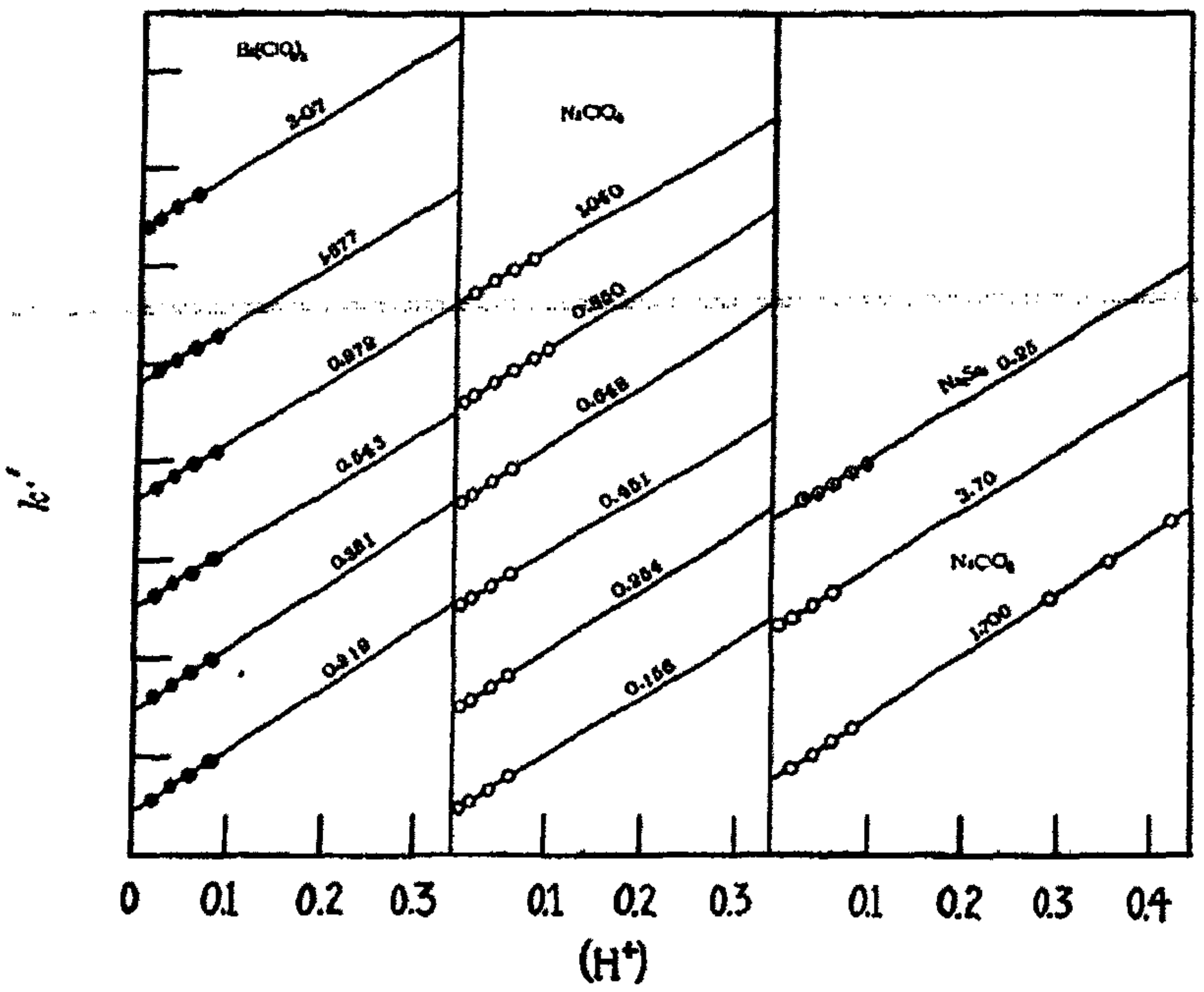


FIG. 1. ABSENCE OF SALT EFFECT ON REACTION 4

Since the curves have been shifted vertically to prevent superposition, numerical values for the ordinates have not been given. For every curve, any value of k' may be found from table 1 if the ionic strength, given above the curve, is used to identify the curve in question.

---

[3] Two factors insure that the salt effect on k_1^0 will not appreciably alter the slopes of the lines in figure 1: at low (H^+) the change in μ_c caused by adding acid is so small that k_1^0 is not sensibly affected; at high (H^+) the contribution of reaction 3 to the absolute rate is relatively small; in the region of intermediate (H^+), both effects are operative.

TABLE 1

Detailed experimental results for figure 1

Sodium iodide–perchloric acid solutions. Temperature, 25°C. Initially (H_2O_2) = 8 × 10^{-4} moles per liter. Average (I^-) = 5.72 × 10^{-3} moles per liter. Values of (H^+) are averages.

SERIES	ADDED SALT	CONCENTRATION OF ADDED SALT	μ_c^*	(H^+)	k'
		moles per liter		*moles per liter*	
2	$Ba(ClO_4)_2$	0.054	0.219	0.02022	0.0563
				0.04130	0.0706
				0.0623	0.0811
				0.0834	0.0964
3	$Ba(ClO_4)_2$	0.108	0.381	0.02030	0.0617
				0.04130	0.0715
				0.0624	0.0860
				0.0834	0.0990
4	$Ba(ClO_4)_2$	0.162	0.543	0.02021	0.0640
				0.04130	0.0773
				0.0623	0.0872
				0.0834	0.1010
5	$Ba(ClO_4)_2$	0.305	0.972	0.02030	0.0730
				0.04130	0.0850
				0.0623	0.098
				0.0834	0.110
6	$Ba(ClO_4)_2$	0.540	1.677	0.02023	0.0936
				0.04130	0.1040
				0.0624	0.1170
				0.0834	0.1290
7	$Ba(ClO_4)_2$	1.004	3.07	0.00760	0.1400
				0.02020	0.1490
				0.04130	0.1610
				0.0624	0.1740
8	$NaClO_4$	0.0985	0.156	0.00763	0.0480
				0.02027	0.0550
				0.04128	0.0670
				0.0624	0.0794
9	$NaClO_4$	0.0197	0.254	0.00767	0.0510
				0.02021	0.0575
				0.04130	0.0698
				0.0623	0.0820
10	$NaClO_4$	0.394	0.451	0.00761	0.0530
				0.02024	0.0600
				0.04130	0.0730
				0.0623	0.0850

TABLE 1—*Concluded*

SERIES	ADDED SALT	CONCENTRATION OF ADDED SALT	μ_c*	(H⁺)	k'
		moles per liter		*moles per liter*	
11	$NaClO_4$	0.591	0.648	0.00764	0.0580
				0.02026	0.0660
				0.04123	0.0790
				0.0623	0.0920
12	$NaClO_4$	0.793	0.850	0.00758	0.0600
				0.02025	0.0680
				0.04126	0.0800
				0.0623	0.0940
				0.0832	0.1070
				0.0998	0.115
13	$NaClO_4$	0.983	1.040	0.02024	0.0730
				0.04129	0.0850
				0.0623	0.0961
				0.0832	0.1085
14	$NaClO_4$	1.643	1.700	0.02030	0.0880
				0.04130	0.1024
				0.0623	0.1152
				0.0834	0.1277
				0.2934	0.2600
				0.3571	0.2990
				0.4202	0.3400
15	$NaClO_4$	3.643	3.70	0.00753	0.1330
				0.02024	0.1410
				0.04130	0.1540
				0.0623	0.1670
16	Na_2SO_4†	0.0644	0.25	0.03048	0.0619
				0.04520	0.0684
				0.0621	0.0775
				0.0800	0.0890
				0.0987	0.0984

* μ_c represents the ionic strength, in concentration units, due to iodide and added salts; its value for each series is given above the curve in figure 1 corresponding thereto.

† Formation of HSO_4^- has been considered in calculating (H⁺); the uncertainty of this correction precluded measurements in more concentrated sodium sulfate solutions.

of reasonable magnitude, reaction 4 is altogether without the exponential salt effect predicted by the Brönsted theory (2). Before these conclusions are discussed, we shall consider briefly the results of a group of experiments designed to reveal whether reaction 4 has appreciable salt effect at low ionic strengths.

In these experiments the iodine formed could be accurately titrated with thiosulfate before any marked concentration change occurred, so that the "method of constant rates" (1, 8) could be employed. To the reaction mixture, at room temperature and containing starch as indicator, thiosulfate solution was added from a buret at the minimum rate that would prevent the appearance of the starch blue, while the flask containing the

TABLE 2

Summary of experimental results in figures 1 and 2, and table 1

SERIES	μ_c*	k_1^0	k_1
$Ba(ClO_4)_2$ as added salt			
1†	0.0572	0.69	10.4
2	0.219	0.77	10.8
3	0.381	0.84	10.7
4	0.543	0.91	10.2
5	0.972	1.08	10.2
6	1.677	1.40	10.3
7	3.07	2.41	10.2
$NaClO_4$ as added salt			
8	0.156	0.75	10.7
9	0.254	0.78	10.5
10	0.451	0.85	10.2
11	0.648	0.93	10.8
12	0.850	1.00	10.3
13	1.040	1.07	10.0
14	1.700	1.33	10.8
15	3.70	2.26	10.5
Na_2SO_4 as added salt			
16	0.25	0.74	10.4
Arithmetic mean of k_1 values			10.4 ± 0.06‡

* μ_c represents the ionic strength, in concentration units, due to iodide and added salt.

† These values were obtained without added salt (see reference 7) and are not plotted in figure 1.

‡ The average error of the mean has been computed from a "least squares" formula; this procedure seems applicable, for the value of k_1 for each series was determined independently of the other data—i.e., no attempt was made to select "best" values of k_1 after all the data were at hand.

mixture was kept in constant motion.[3] The thiosulfate consumed in a minute measures the rate at which iodide is oxidized in reaction 1; from this rate, $k'/(I^-)$ may be calculated. Values thereof obtained at different values of (H^+) have been plotted against (H^+) in figure 3; in table 3 the results are summarized.

The results in table 3 demonstrate that this experimental method is capable of less accuracy than the "analytical method" (7) employed to obtain the data in table 1; further, since reaction 4 is responsible, on the average, for only one-tenth of the absolute rate, experimental errors will appear greatly magnified in k_1. We believe, however, that the large number of experiments tends to compensate these inaccuracies; and since the results

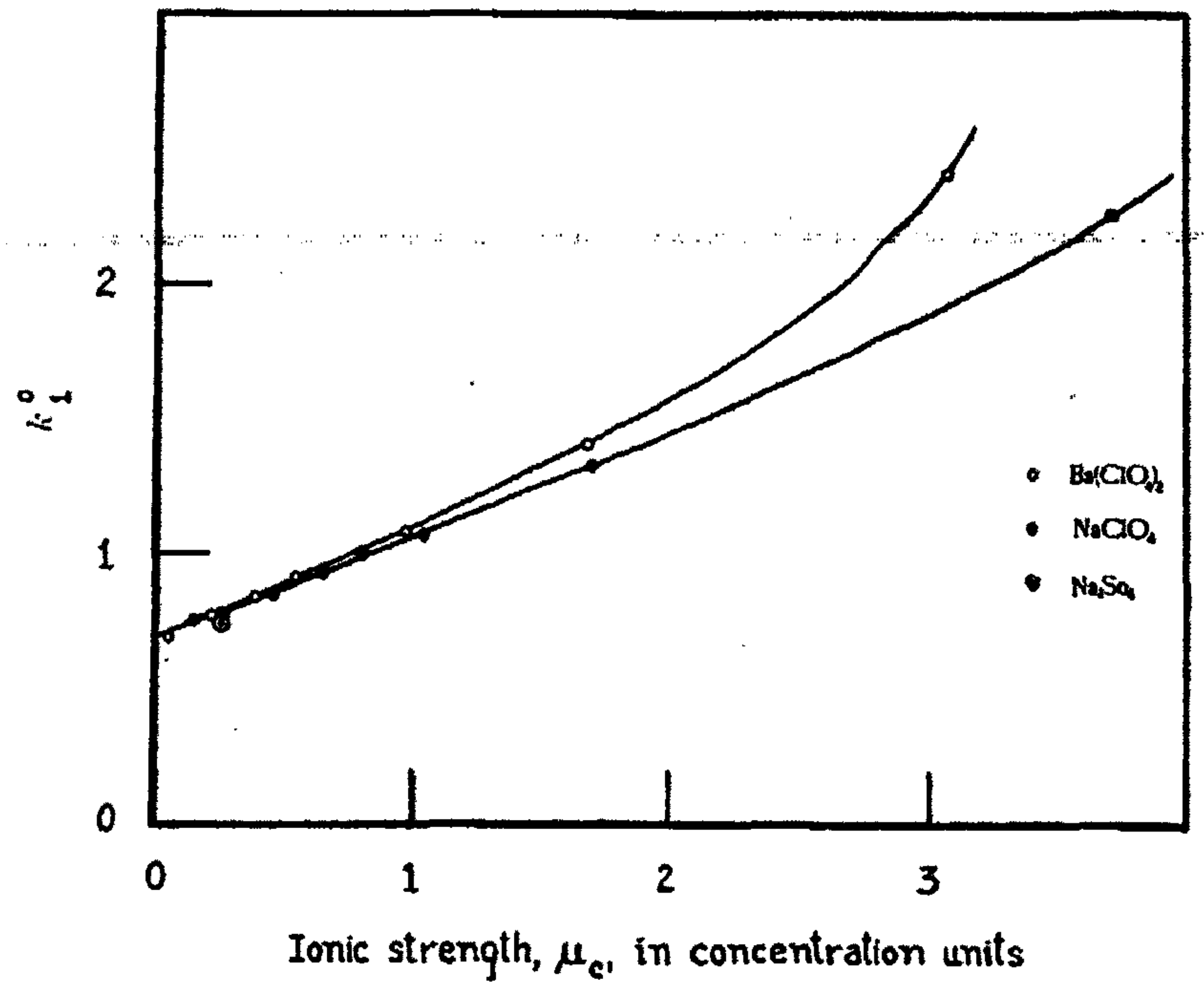


FIG. 2. SALT EFFECT ON REACTION 3
(Cf. table 2)

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[3] Gradual addition of the thiosulfate so that no great excess of it is ever present seems preferable to initial addition of the whole amount, for its oxidation by the hydrogen peroxide is thus greatly reduced. (Cf. Abel: Monatsh. **28**, 1239 (1907).) This oxidation is accelerated somewhat by hydrogen ion; the difference between the k_1 values of table 2, and 10.4, the value from table 1, may conceivably be due to some reaction like this.

Our experimental method is a modification of that first used by Harcourt and Esson (Phil. Trans. Roy. Soc. **157**, 117 (1867)).

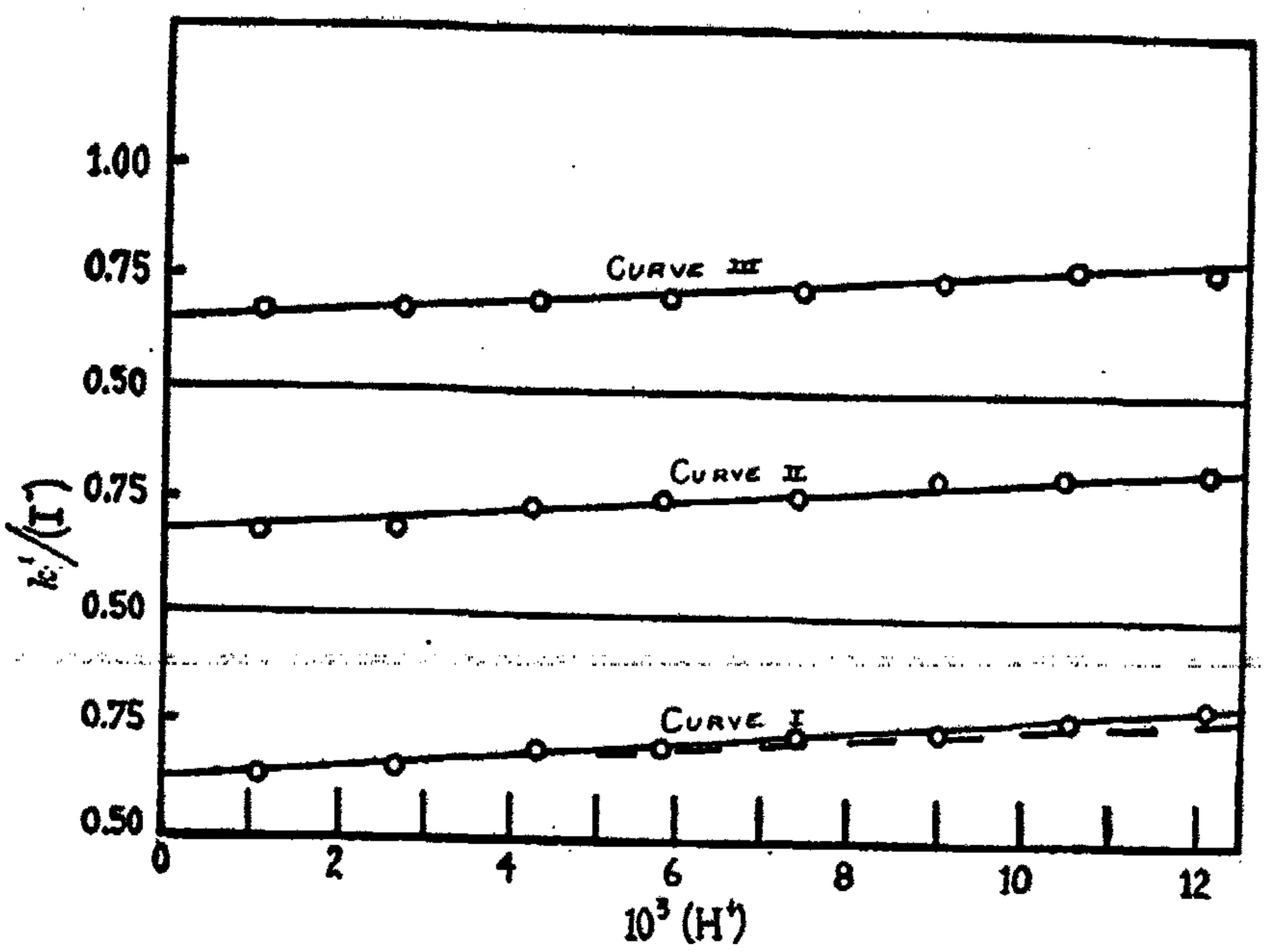

FIG. 3. ADDITIONAL SALT EFFECT MEASUREMENTS

Cf. table 3. The radius of the circles corresponds to a change in $(k'/(I^-))$ of 0.02.

TABLE 3

Data for experiments of figure 3

$(H_2O_2) = 1.23 \times 10^{-2}$ moles per liter; (H^+) variable

SERIES NO.	$(I^-) \times 10^3$	$(NaClO_4)$	k_1^0 (23°)	k_1 (23°)	k_1^0 (25°)	k_1 (25°)
I	1.06	0.00	0.63	11.7	0.74	13.2*
II	1.05	0.113	0.68	12.3	0.79	13.8
III	1.06	0.568	0.65	11.7	0.76	13.2

Corresponding table 1 values: $k_1^0 = 0.69$(I), 0.75(II), and 0.89(III); $k_1 = 10.4$ (all three series).

*0.005 is an average value for the ionic strength of Curve I, figure 3. The dotted line below this curve has been drawn through $k'/(I^-)$ values, each corrected for the positive salt effect on k_1^0. Only for the point at highest acid is this correction, which was determined in additional experiments, appreciably larger than the experimental error; the dotted line gives $k_1 = 12$, which is *lower* than the values at higher ionic strengths. (Did the Brönsted theory apply, it should be *higher*.) We have given the uncorrected value in table 1 because the correction is itself uncertain. Since μ_c does not change greatly along Curves II and III, a similar correction need not be applied.

are self-consistent, we do not hesitate to offer them as confirmatory evidence for the conclusion that reaction 4 is without salt effect. Emphasis should be placed, not on the difference between 13 (the approximate table 3 value of k_1) and 10.4 (the accurate table 1 value), but on the fact that the table 3 values agree with each other. Although the experimental error is rather large (± 10 per cent seems a fair estimate), it is probably not over one-fourth the change in γ^2 over the range of ionic strengths covered in table 3. We must conclude, therefore, that the experiments of figure 3, covering ionic strengths from $\mu_c = 0.005$ (see footnote to table 3) to $\mu_c = 0.5$, furnish no evidence for the exponential salt effect predicted by the Brönsted theory.

DISCUSSION OF RESULTS

In discussing the experimental results we shall employ a terminology differing slightly from what is usual.[4]

An inspection of figure 2 makes evident that, below $\mu_c = 2$, $k_1{}^0$ may be considered a linear function of the ionic strength. As is well known, such an effect may be interpreted as an equilibrium salt effect if the *intimate mechanism*

$$\text{Rapid equilibrium: } H_2O_2 + I^- \rightleftarrows H_2O_2\cdot I^- \qquad (3a)$$

$$\text{Rate-determining: } H_2O_2\cdot I^- \rightarrow H_2O + IO^- \qquad (3b)$$

is assumed for reaction 3: the concentration of $H_2O_2\cdot I^-$ could vary linearly with the ionic strength, for I^- and this complex each carry a single negative charge and therefore have similar activity coefficients. (Thus, for series 5, table 1, ($H_2O_2\cdot I^-$) would be $\frac{1.08}{0.69}$ times as large as for series 1.) The curvature, which becomes pronounced as μ_c increases above 2, might well be due to a superimposed medium effect, more marked with barium perchlorate; this superimposed effect might be responsible also for the steeper

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[4] By the general term "salt effect" we understand the effect, to a first approximation similar for all electrolytes, on the rate of a reaction of changing the ionic strength. (Skrabal (Z. physik. Chem. 3B, 247 (1929)) prefers the more accurate term "electrolyte effect," which he has been using for many years.) Three kinds of salt effects may now be recognized: *equilibrium salt effects*, caused by the shift in an equilibrium, which accompanies a change in ionic strength and alters the concentration of a substance involved in a rate-determining step; *kinetic salt effects* to which no definite cause can be assigned, but with which the various attempts to introduce activity coefficients into rate laws (the activity theories of reaction rate) are principally concerned; and *medium effects*, which result when electrolyte addition has been so large that the reaction now proceeds in what is virtually a new solvent. There seems to be no sharp line of demarcation between medium effects and pronounced kinetic salt effects.

Our "equilibrium" salt effect is identical with the "secondary kinetic" salt effect of Brönsted (2), while we have omitted "primary" in naming his "primary kinetic" salt effect.

slope of the barium perchlorate line in figure 2. The results in this figure do not differ markedly from some obtained by Harned and his collaborators (3, 4, 5, 6) by a different experimental method.

When we come to consider reaction 4, one thing is immediately obvious; the experimental results cannot be interpreted by the use of any activity theory of reaction rates, for k_1 is independent of the ionic strength, and the introduction of thermodynamic activity coefficients into the rate law would therefore destroy the constancy experimentally observed. The discovery of additional cases of this kind would furnish strong evidence for the belief that no theory leading to rate laws that involve thermodynamic activity coefficients can hope to prove generally valid.

From another point of view, also, this absence of salt effect, so unexpected in the light of past experience, is disturbing. It has been shown (7) that

$$k_1^0 = 4.91(10^9)e^{\frac{-13,400}{RT}}, \text{ from 0 to 50°C.} \tag{5}$$

and

$$k_1 = 4.58(10^8)e^{\frac{-10,450}{RT}}, \text{ from 0 to 40°C.} \tag{6}$$

Reactions 3 and 4 thus possess nearly identical heats of activation and nearly identical Arrhenius constants; this confirms the expectation, based on the fact that a single hydrogen ion represents the only difference apparent between these two rate-determining steps, that their intimate mechanisms will be very similar. In this event, however, we would have two closely related reactions, of which one (reaction 3) exhibits a normal salt effect, while the other shows none—a state of affairs not at all reasonable. In particular, if reaction 4 is to have an intimate mechanism

Rapid equilibrium: $H_2O_2 + I^- \rightleftharpoons H_2O_2 \cdot I^-$ (4a) also (3a)

Rate-determining: $H_2O_2 \cdot I^- + H^+ \rightarrow H_2O + HIO$ (4b)

patterned after equations 3a and 3b, we would have to make the unwelcome assumption that the linear positive salt effect (which, together with the low Arrhenius constant, 4.91 (10^9), supports equations 3a and 3b) found for reaction 3 is somehow miraculously compensated in reaction 4b. (Thus, if reaction 4b in the above scheme takes place, it—like reaction 3b—should be influenced by the $\frac{1.08}{0.69}$-fold increase in ($H_2O_2 \cdot I^-$) for series 5, table 1, over that for series 1.) Of course, equations 4a and 4b do not exhaust the possibilities; the statistically complex process we recognize as reaction 4 may be formulated differently, but we have found no formulation that can explain the absence of any appreciable salt effect for the reaction.

If results like ours are not restricted as to the type of reaction for which they occur, it would seem advisable to treat salt effects, with the exception of those involving known equilibria, from a more empirical point of view than is at present customary.

CONCLUSION

The salt effect on the rate at which hydrogen peroxide is reduced in acid solution by iodide ion has been studied over a large range of ionic strengths, sodium and barium perchlorates serving as added salts. Of two rate-determining steps proceeding simultaneously and independently, the one (a second-order reaction involving hydrogen peroxide and iodide ion) exhibits the linear type of salt effect to be normally expected, while the other (a third-order reaction involving hydrogen peroxide, and hydrogen and iodide ions) is without any appreciable salt effect whatever. This behavior contradicts the bulk of past experience and is irreconcilable with any activity theory of reaction rates; it suggests that salt effects in general might perhaps be profitably treated from a point of view more empirical than that now customary. An alternative terminology for the discussion of salt effects has been proposed.

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PHYSICOCHEMICAL STUDIES ON GUM ARABIC SOLUTIONS

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Received November 28, 1933

I. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF ARABIC ACID AND ITS SALTS

There are several reasons why gum arabic serves as an especially satisfactory colloid for use in experiments of the nature to be described in the following papers. It forms definitely colloidal solutions in water. It is easily prepared from the commercially obtainable sorts in the manner described below and the various preparations, using commercial gum from the same source, i.e., Sudan gum, have been found, in the experience of the author, to be identical in their properties. The gum can be electrodialyzed until it is practically free of ash, forming a fairly strong acid, the equivalent weight of which does not vary appreciably from sample to sample. This indicates that all salt-forming groups (acid groups) in the colloidal micella are available to react within a very short period of time with the added alkali (in contrast to silicic acid solution, for example). The arabic acid is stable against hydrolysis by its own hydrogen ions (agar, for instance, is partially hydrolyzed upon electrodialysis). The acid and all of its salts are soluble in water in all proportions, an advantage over soap solutions where many salts and the free acids are generally insoluble in water. Solutions of the arabic acid or its salts are relatively stable against attack by microörganisms, no change in the solutions being detectable after standing at room temperature without preservative for days. And finally, it has no isoelectric point, i.e., is not amphoteric. It acts always as an acidic substance. The acid group in the gum arabic is probably a carboxyl group. The electrodialyzed gum contains no sulfur or phosphorus.

The purified gum is prepared by dissolving the sorts in water to form a 5 to 10 per cent solution which is filtered, and enough hydrochloric acid then added to make the solution about 0.1 *N* acid. Alcohol is then added until the gum is precipitated as a white granular mass, which is separated from the mother liquor by filtration. The gum is redissolved and reprecipitated twice, and then partially dried *in vacuo* to remove most of the alcohol. It is then dissolved in a small amount of water and electrodialyzed in a three-compartment cell with frequent changes of water in the electrode compartments until no further change in conductivity of the gum solution is observed. Cellophane membranes are used. The electrodialysis requires about a week to go to completion, during which time the current is maintained below 0.3 ampere in order to prevent too much heat from being developed in the solution. Toward the last, the current drops off to a very small value, owing to the absence of electrolytes in the electrode compartments. Considerable calcium hydroxide appears in the cathode chamber during the early stages of electrodialysis. The final solution of the gum is strongly acid (approximate pH = 2.0), and its ash content has dropped to about 0.05 per cent of the dry weight of the gum. Its titration curve is that of a fairly strong acid. One gram of the acid requires 85×10^{-5} equivalents of base to neutralize it, indicating its equivalent weight to be 1175. This value is identical with that obtained by Thomas and Murray (5) upon a sample of gum similarly prepared.

The various salts of arabic acid used in the following experiments were prepared by neutralizing the acid with the hydroxides of the metals the salts of which were desired, and drying the solutions *in vacuo* at 70°C., after which the salts were kept dry until used. The acid itself was not prepared in the dry form, but its concentration in a stock solution was determined and this solution used wherever experiments on the free acid were made.

Specific conductivity measurements were made upon the arabic acid and its salts at 25°C., using a conductivity cell of the Washburn type, the cell constant being 0.3560. The usual Wheatstone bridge arrangement was used with earphone detector and an alternating current of 1000 cycles. The solutions were made up on the weight basis, the concentrations being shown in the tables as the number of grams of dry colloid per 1000 grams of water. Triple distilled water was used as solvent, this having a specific conductivity value of 2 to 4×10^{-6} mhos.

The specific conductivities of the solutions, as given in the tables, have been corrected for the conductivity of the water and, upon the assumption that conductance through the volume occupied by the micellae would be negligible, the specific conductivities of the solutions are corrected for the volume occupied by the colloid in the solution. Where μ is the fraction of the total volume of the solution which is occupied by the gum, the observed electrical resistance in the conductivity cell must be multiplied by the factor, $1 - \mu$, in order to find the resistance offered by the intermicellar liquid, i.e., the true resistance of the solution. The value, μ, may be calculated according to the equation

$$\mu = 1 - \frac{1000s}{(1000 + a)H}$$

where s = the specific gravity of the solution at 25°C., H = that of water at 25°C., and a = the number of grams of the colloid dissolved in 1000 g. of water. This correction is of the order of 6.4 per cent in the most concentrated solution used (i.e., 100 g. of colloid in 1000 g. of water) and rapidly decreases in magnitude as dilution increases.

The equivalent volumes of the solutions are calculated as the number of cubic centimeters of solution containing one equivalent of the colloid electrolyte, according to the equation

$$V = \frac{1000 + a}{85 \times 10^{-6} \times s \times a}$$

In order to obtain the equivalent volume of the solution after correction for the volume occupied by the colloidal micellae (as appears in the tables), the value V must be multiplied by the above factor, $1 - \mu$, i.e.,

$$V_e = V \times (1 - \mu)$$

The equivalent conductivities, $\Lambda = V_e \times \kappa$, for the acid and for five salts, viz., potassium, sodium, lithium, calcium, and strychnine salts of the acid, are given in tables 1 and 2 and are plotted in figure 1 against the log of V_e, the equivalent volume. The acid shows a maximum at very high dilution, while the salts of the alkali and alkaline earth metals show curves similar to those found by McBain and his students (3) for the salts of the high molecular weight fatty acids, i.e., soaps. With all these salts of arabic acid a minimal equivalent conductivity is found at a concentration of about 0.0025 equivalent per liter (log V_e = 5.6). Besides this similarity of form between the equivalent conductivity–concentration curves of arabic salts and the soaps, there are several marked dissimilarities which should be pointed out. The minimum occurs with soap solutions at an equivalent concentration of 0.1 as compared with 0.0025 for the acacia salts. Also the equivalent conductivities of soaps are unexpectedly high, being between two and three times the mobility value of the cation alone, while with the acacia salts the equivalent conductivities of the salts of the alkali metals are only of the order of the mobilities of the corresponding cations. In the case of the calcium salt it is much lower than that of calcium ion (if complete dissociation of the salt were to be assumed).

From the data obtained on the alkali metal and calcium salts alone, it is possible to offer various possible explanations for the form of curve shown. Although the arabic acid acts as a fairly strong acid and the alkali metal salts of even weak acids are nearly completely ionized at the equivalent concentrations studied in these experiments, we could assume something less than 100 per cent ionization and could then apply the explanation offered by McBain for the data obtained from the soap solutions. That is, the increase in conductivity for concentrations lower than that at

TABLE 1

Conductivity data on arabic acid at varying dilutions

a	s	V_e	κ corrected $\times 10^5$	Λ_{acid}	pH	$[H^+]$ $\times 10^5$	V_{H^+}	Λ_{H^+}	$[T]$	$[HA] = [T] - [H^+]$ $\times 10^5$	$\frac{[A^-]}{[HA]}$	$-\log\frac{[A^-]}{[HA]}$	$pK = pH - \log\frac{[A^-]}{[HA]}$	α
grams		*cc.* $\times 10^{-3}$					*cc.* $\times 10^{-3}$		*equiv.* $\times 10^5$					
100	1.030	11.80	260.4	30.71	2.082	828.0	120.75	315.0	7961	7133	0.1161	0.935	3.017	0.1041
80	1.024	14.76	231.6	34.18	2.125	750.0	133.33	309.0	6450	5700	0.1316	0.881	3.006	0.1163
60	1.018	19.70	196.2	38.62	2.195	638.0	156.80	307.5	4895	4257	0.1499	0.824	3.019	0.1303
50	1.015	23.61	175.1	41.35	2.245	568.5	176.00	308.0	4106	3537	0.1608	0.794	3.039	0.1385
40	1.012	29.51	151.0	44.58	2.304	496.2	201.60	304.8	3307	2811	0.1765	0.753	3.057	0.1501
25	1.0075	47.22	108.2	51.05	2.441	362.0	276.30	299.0	2090	1728	0.2094	0.679	3.120	0.1732
20	1.006	59.00	89.8	53.00	2.520	302.0	331.10	297.5	1677	1375	0.2197	0.658	3.178	0.1802
10	1.003	118.10	52.55	62.07	2.751	177.4	563.80	296.2	843.5	666.1	0.2760	0.575	3.326	0.2102
5.0	1.0015	236.10	29.35	69.30	2.995	101.2	989.00	290.5	423.5	322.3	0.3139	0.503	3.498	0.2391
2.5	1.000	472.00	16.07	75.80	3.255	55.55	1800.0	289.5	212.0	156.5	0.3550	0.450	3.705	0.2620
1.25	0.998	944.00	8.66	81.75	3.531	29.43	3400.0	294.5	106.0	76.57	0.3845	0.415	3.946	0.2778
0.625	0.997	1891.50	4.59	86.80	3.805	15.66	6390.0	293.2	52.87	37.21	0.4210	0.376	4.181	0.2962
0.3125	0.997	3788.0	2.35	89.00	4.108	7.80	12825.0	301.2	26.40	18.60	0.4190	0.378	4.486	0.2955
0.1563	0.997	7570.0	1.15	87.10	4.416	3.84	26050.0	299.5	13.21	9.37	0.4095	0.387	4.803	0.2906
0.0714	0.997	16560.0	0.43	71.20	4.867	1.36	73600.0	316.0	6.04	4.68	0.2905	0.537	5.404	0.2251
H_2O	0.997		0.21											

a = grams of colloid dissolved in 1000 g. of water.
s = specific gravity of the colloid-containing solution.
V_e = equivalent volume of the solution.
κ = specific conductivity of solution at 25°C.
Λ = equivalent conductivity of solution.
V_{H^+} and Λ_{H^+} = equivalent volume and equivalent conductivity on basis of hydrogen-ion concentration.
$[H^+]$, $[A^-]$, etc. = concentration per liter of solution.
pK = negative logarithm of the dissociation constant.
α = degree of ionization of the colloid electrolyte.

TABLE 2

Conductivity data on neutral salts of arabic acid at varying dilutions

a	s	V_e	LOG V_e	POTASSIUM ARABATE		SODIUM ARABATE		LITHIUM ARABATE		CALCIUM ARABATE		STRYCHNINE ARABATE	
				$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ
		cc. × 10^{-3}											
50	1.0165	23.60	4.373	250.00	59.00	182.50	43.10	149.20	35.25	106.10	25.05	78.80	18.60
40	1.0135	29.55	4.470					121.80	36.00				
30	1.0100	39.35	4.595							61.00	24.00	48.40	19.05
25	1.0084	47.20	4.674	123.70	58.35	91.80	43.30						
20	1.0067	59.10	4.772					60.95	36.05	38.75	22.90	33.10	19.56
10	1.0033	118.10	5.072	46.40	54.80	35.14	41.50	29.83	35.25	18.00	21.27	17.28	20.40
5	1.0016	236.00	5.373	22.25	52.55	17.06	40.35	14.69	34.70	8.55	20.20	8.97	21.17
2.5	1.0000	472.00	5.674	10.98	51.82	8.50	40.12	7.26	34.30	4.35	20.55	4.74	22.38
1.25	0.998	944.50	5.976	5.54	52.30	4.36	41.20	3.76	35.50	2.25	21.25	2.55	24.10
0.625	0.997	1891.50	6.277	2.88	54.45	2.28	43.12	2.02	38.20	1.22	23.07	1.35	25.55
0.3125	0.997	3788.10	6.578	1.51	57.20	1.24	46.95	1.09	41.30	0.70	26.50	0.79	29.90
0.156	0.997	7570.00	6.879	0.82	62.10	0.67	50.70						
H_2O	0.997			0.35		0.40		0.23		0.24			

which the minimum is observed would arise from a continuous increase in degree of ionization with increased dilution, while the increase in conductivity for concentrations higher than that at which the minimum is found would result from an increase in the degree of aggregation of the colloidal anion accompanied by a marked increase in the charge density on the sur-

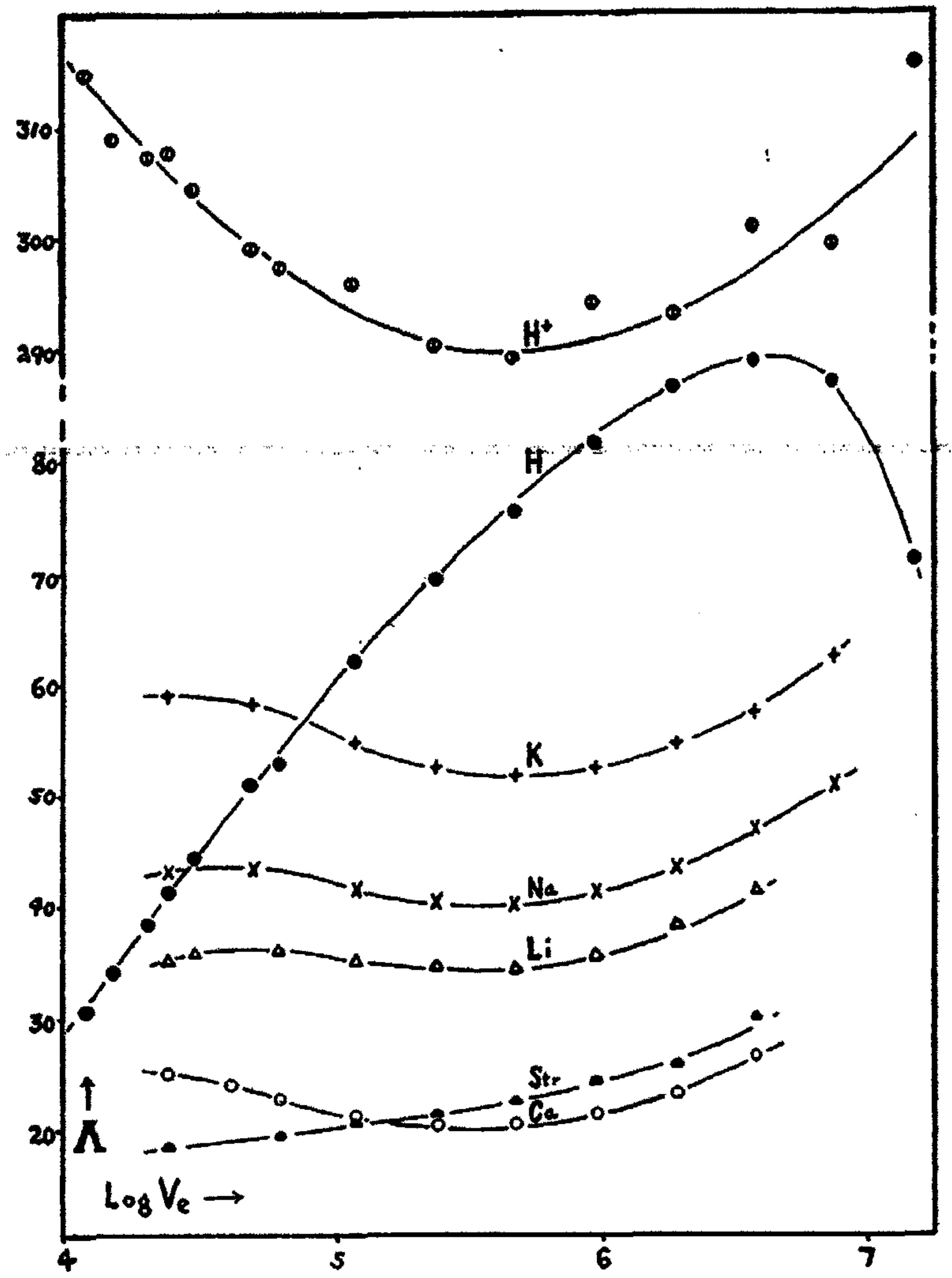

FIG. 1. CURVES SHOWING THE VARIATION OF THE EQUIVALENT CONDUCTIVITY (Λ) OF SOLUTIONS OF ARABIC ACID AND ITS VARIOUS SALTS, WITH CHANGE IN EQUIVALENT VOLUME (V.)

Curve marked (H^+) shows the equivalent conductivity on the basis of the ionized fraction of the acids, while curve marked (H) shows the equivalent conductivity on the basis of total acid present in solutions.

face of the micella (decrease in surface area per unit charge). A correspondingly higher migration velocity of the micella would result, this accounting for the increased transference of electric current.

Again, assuming less than complete ionization of the alkali metal salts of arabic acid and explaining the increase in Λ with increased dilution as above, it is possible that the increase in Λ with increased concentration results not because of increased agglomeration of the anionic carrier but because of an increase in the percentage of total current carried by surface conducting ions. Surface conductance measurements on glass and cellulose surfaces indicate that the ions present in the region of the interface can move more freely through the surface region under the influence of an electric field than they can through the bulk of the solution. If, in the present case, owing to greater concentration of the colloid, the number of contacts between micellae increased to a large degree, it is possible that a marked increase in the current carried by the solution might result when surface conductance took place at the instant of contact between the micellae. That agglomeration would follow such contacts between the micellae does not necessarily follow, because these hydrophilic colloids do not depend upon their electric charge to maintain their stability.

A third explanation of these data, and one which seems to fit the additional data obtained upon the acid and its strychnine salt, arises from conclusions drawn by Lewis (2) concerning the validity of Kohlrausch's assumption of constant ion mobility with change in concentration of the electrolyte. Lewis, from an analysis of existing data, showed that the transference number of an ion (i.e., the fraction of total current carried by that ion) may change radically with change in electrolyte concentration of the solution, and therefore the relative mobility of the ions must be changing with concentration. This change becomes most noticeable when the differences in mobility of the two ions involved are markedly unequal. Kohlrausch's assumption of constant ion mobility is therefore not strictly true, and it is possible that the mobility of an ion may vary with the concentration. Lewis found a minimum to exist in the transference number–concentration curve for several ions in true solution. If the large fraction of the current carried by an electrolyte is carried by one ion, the transference number of the other ion being very low, it is to be expected that the changes in mobility of the ion of higher transference number would be noticeably reflected by similar changes in the Λ–concentration curve of the electrolyte. Since, too, the relative change in mobilities with concentration of the two ions is more marked the greater the difference in the absolute mobilities of the ions, it is to be expected that as the relative mobilities of the ions became nearer 1 (i.e., as the absolute mobilities became more nearly equal), the Λ–concentration curve would no longer show evidences of those influences at work in the solution.

The mobility of the arabate ion is not known, but its transference number must be very low, as evidenced by the fact that the equivalent conductivities of the lithium, sodium, and potassium salts are somewhat lower than the values to be expected from the cation alone if the salt were 100 per cent ionized. That these salts are nearly totally ionized is indicated by the fact that the equivalent conductivity of the hydrogen ions, in the experiments with the acid, shows a change with concentration similar to that of the salts. The curve for the equivalent conductivity of the acid on the basis of hydrogen-ion concentration, lies below the usually accepted mobility value of hydrogen ion (i.e., 315), a distance which is relatively equal to the distance that the curves from the salts lie below the mobility value of their respective cations. The curve marked H^+ in figure 1 is that plotted from values of Λ_{H^+} for the acid calculated on the basis of hydrogen-ion concentrations at the various dilutions. The hydrogen-ion concentrations were determined electrometrically upon the same solutions that were used for the conductivity experiments. It is seen from the curve that current carried by equal amounts of ionized acid is at a minimum in the same region of concentration (of total colloid) as that in which a minimum is observed in the equivalent conductivities of the salts. If we can assume that electrometric measurements of hydrogen-ion concentration with a hydrogen electrode give a correct measure of the hydrogen-ion activity in the solution, we have here definite proof that the cation mobility is changing with concentration of the colloid electrolyte. In this case the greater part of the current must be carried by the hydrogen ions. If the same is true of the lithium, potassium, and sodium salts it is evident that these must be ionized to a very great extent. The same cannot be said of the calcium salt. Here the degree of ionization must be of the order of 50 per cent.

It can be assumed then that the mobility of the arabate ion is low. Since the effect of concentration upon mobility of the cation associated with the arabate ion should, according to this theory, become less apparent as the mobilities of the cations approached that of the arabate ion, it is proper that we should observe that the Λ–concentration curve tends to flatten out (i.e., the minimum becomes less pronounced), as the mobility of the cation decreases. The curve for the H^+ salt shows a very deep cusp on the curve, while that of the lithium salt is nearly flat, though still showing a distinct minimum. With the, presumably, slow moving organic cation, strychnine, the cation mobility has reached a sufficiently low value so that there no longer exists a minimum in the Λ–concentration curve for its salt with arabic acid, that is, there is not sufficient difference between the mobilities of the arabate and strychnine ions to cause variation in the mobilities of the cation to such a degree as to become apparent in the Λ-concentration curve for this salt.

This theory does not rule out the possibility of a reversible agglomeration of the micellae taking place as the concentration increases. It does, however, postulate that the variation in the Λ–conductivity curves is largely due to variation in the absolute mobility of the cations which, in the case of this particular colloid electrolyte, appear to act as conductors for almost all of the current which passes through the solution. The maximum in the Λ–concentration curve for the acid coincides closely with a maximum in percentage ionization as indicated from hydrogen-ion measurements. An explanation of this observation will be given in the succeeding section in terms of the existence of a reversible polymerization or peptization occurring with change in concentration of the acid in solution.

II. THE DISSOCIATION "CONSTANT" OF ARABIC ACID

When an electrodialyzed gum arabic solution is titrated with an alkali and the course of the hydrogen-ion concentration in the solution followed electrometrically with a bubbling hydrogen electrode, the titration curve so obtained is found to be that of a fairly strong acid. The curve is smooth like that of any monobasic acid, although the molecular (or micellar) weight of the arabic acid must be many times its equivalent weight. The neutralization equivalent of the acid does not change with dilution and is equal to 85×10^{-5} equivalents per gram of the acid. The time required for equilibrium to be attained after addition of an increment of alkali is only of the order of time needed for complete mixing of the solutions. It would appear, therefore, that the acid (replaceable) hydrogens of the colloid exist at the surface of the micellae and are readily available to react with the added alkali. Certainly no part of the colloid exists in the form of the acid anhydride, which requires hydrolysis to take place before reaction with the alkali can occur. (As is the case with a silica gel micella, where the inner portion of the micella consists of SiO_2 which must hydrolyse to H_2SiO_3 before reaction with sodium hydroxide to form the sodium silicate.) Thomas and Murray (5) showed that no further alkali was bound beyond a pH of 7, i.e., all acid hydrogens of the acid react with the alkali before pH = 7 is reached.

Since the acid, which obviously cannot be a monobasic acid, shows a titration curve essentially that of a monobasic acid, it is necessary to picture the acid hydrogens of the acid as being so far apart in the molecule that the ionization of one group has practically no intramolecular influence upon the tendency of the other groups to ionize, or else that every ionizable hydrogen present has a dissociation constant somewhat different from every other one and that these dissociation constants for the various acid groups are rather uniformly distributed throughout the buffer range of the acid. In the first case, the calculation of the dissociation constant of the acid as a monobasic acid would be allowed. In the second case such a calculation would mean nothing, except that the constant so obtained would refer to an average dissociation tendency of all the acid groups present in the acid.

The dissociation "constant" of arabic acid has been calculated, in this paper, upon the assumption that the acid acts as a monobasic acid, from dilution data on the acid and from the titration curves at various dilutions.

TABLE 3

Titration data for arabic acid at two concentrations

NaOH PER GRAM	pH	$[H^+]$ $\times 10^5$	$[T]$ $\times 10^5$	$[Na^+]$ $\times 10^5$	$[A^-] = [Na^+] + [H^+]$ $\times 10^5$	$[HA] = [T] - [A^-]$ $\times 10^5$	RATIO $[A]/[HA]$	LOG RATIO	pK
				50 g. acid per 1000 g. water					
equiv. $\times 10^5$									
0	2.24	575.0	4250	0	575	3675	0.1565	−0.805	3.05
7.08	2.45	355.0	4250	354	709	3541	0.2001	−0.699	3.15
14.17	2.64	230.0	4250	708	938	3312	0.2831	−0.548	3.19
21.25	2.81	155.0	4250	1062	1217	3033	0.4010	−0.397	3.21
28.33	3.00	100.0	4250	1417	1517	2733	0.5550	−0.256	3.26
35.41	3.15	70.8	4250	1771	1842	2408	0.7550	−0.116	3.27
42.50	3.34	45.8	4250	2125	2171	2079	1.045	+0.019	3.32
49.58	3.50	31.6	4250	2480	2512	1738	1.445	+0.160	3.34
56.66	3.68	20.9	4250	2833	2854	1396	2.042	+0.310	3.37
63.73	3.90	12.6	4250	3187	3200	1050	3.048	+0.484	3.42
70.82	4.13	7.41	4250	3541	3548	702	5.055	+0.704	3.43
77.91	4.60	2.50	4250	3895	3898	352	11.070	+1.045	3.55
85.00	7.00		4250	4250	4250				
				0.625 g. acid per 1000 g. water					
0	3.82	15.12	53.1	0	15.1	38.0	0.398	−0.401	4.22
14.17	4.11	7.77	53.1	8.85	16.6	36.5	0.455	−0.342	4.45
28.33	4.43	3.72	53.1	17.71	21.4	31.7	0.675	−0.170	4.60
42.50	4.95	1.12	53.1	26.60	27.7	25.4	1.091	+0.038	4.91
56.66	5.39	0.408	53.1	35.40	35.8	17.3	2.070	+0.316	5.07
70.82	6.01	0.098	53.1	44.30	44.4	8.7	5.110	+0.708	5.30
85.00	7.00		53.1	53.10	53.1				

These calculations are given, with the data from which the values were calculated, in tables 1 and 3 and are shown graphically in figures 2 and 3.

The values obtained for the acid at various dilutions were calculated from measurements on the same solutions as those used for conductivity measurements, where the hydrogen-ion concentrations were determined electrometrically. The pK (i.e., the negative logarithm of the dissociation constant) was calculated according to the equation

$$pK = pH - \log \frac{[A^-]}{[HA]}$$

the value of [A^-] being taken as equal to the measured [H^+], and [HA] being taken as equal to the total equivalent concentration of the acid [T] minus [H^+]. The degree of ionization of the acid at the various dilutions is also calculated as

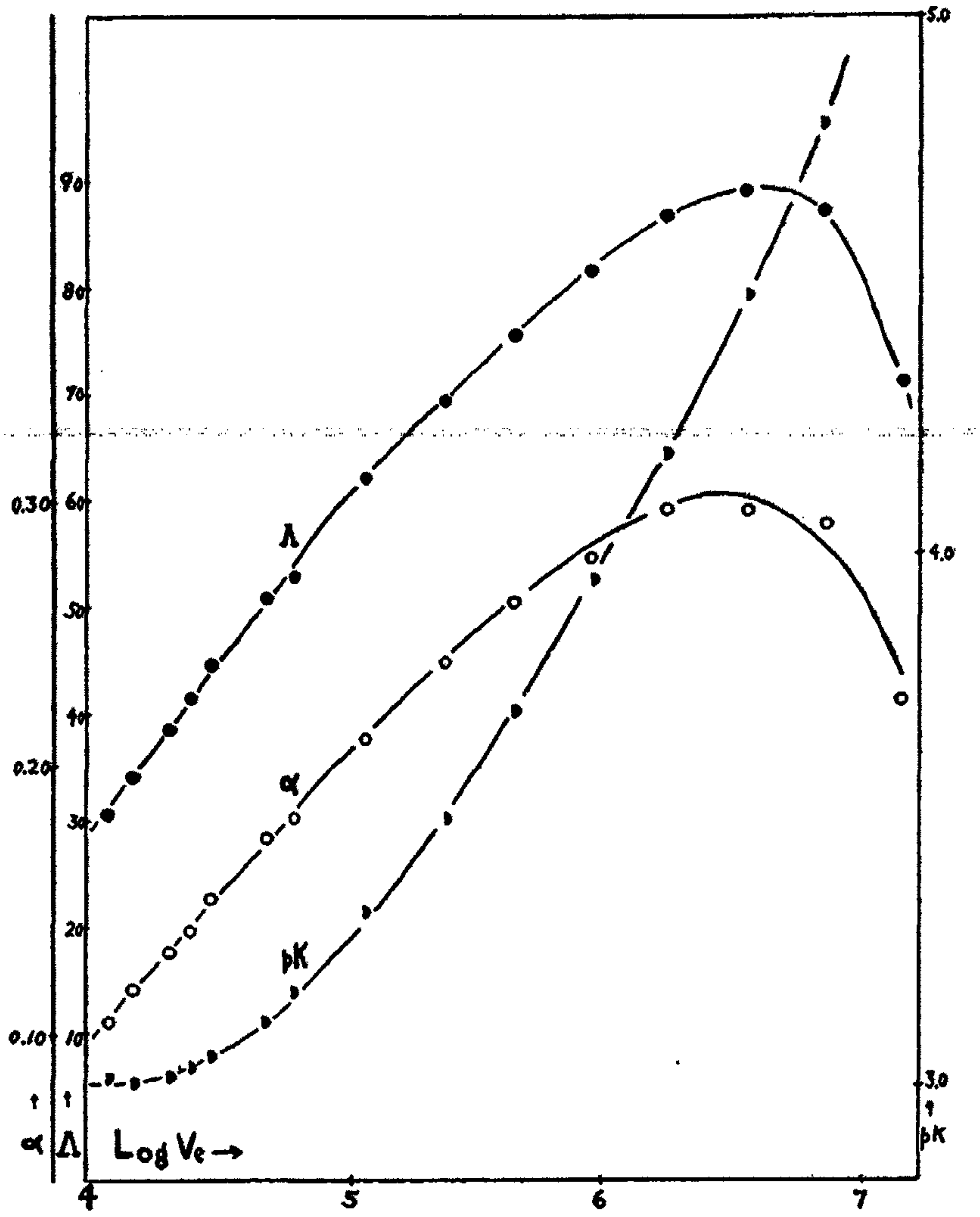

Fig. 2. Curves Showing the Manner in Which the Equivalent Conductivity (Λ), the Degree of Ionization (α), and the Dissociation "Constant" (K) of the Acid (Plotted as the Negative Logarithm of K) Vary with the Concentration of the Solutions of the Acid (Plotted as the Logarithm of the Equivalent Volume (V_e))

$$\alpha = \frac{[H^+]}{[T]}$$

In figure 2 it is seen that α reaches a maximum at about the same concentration of the acid at which the equivalent conductance, Λ, of the acid reaches a maximum. Also it is seen that the pK value of the acid at concentrations higher than 50 to 60 g. per 1000 g. of water (equivalent concentration of 4 to 5 $\times$ 10^{-2}) becomes fairly constant in the neighborhood of 3 ($K = 1 \times 10^{-3}$), but with increased dilution the value of pK increases

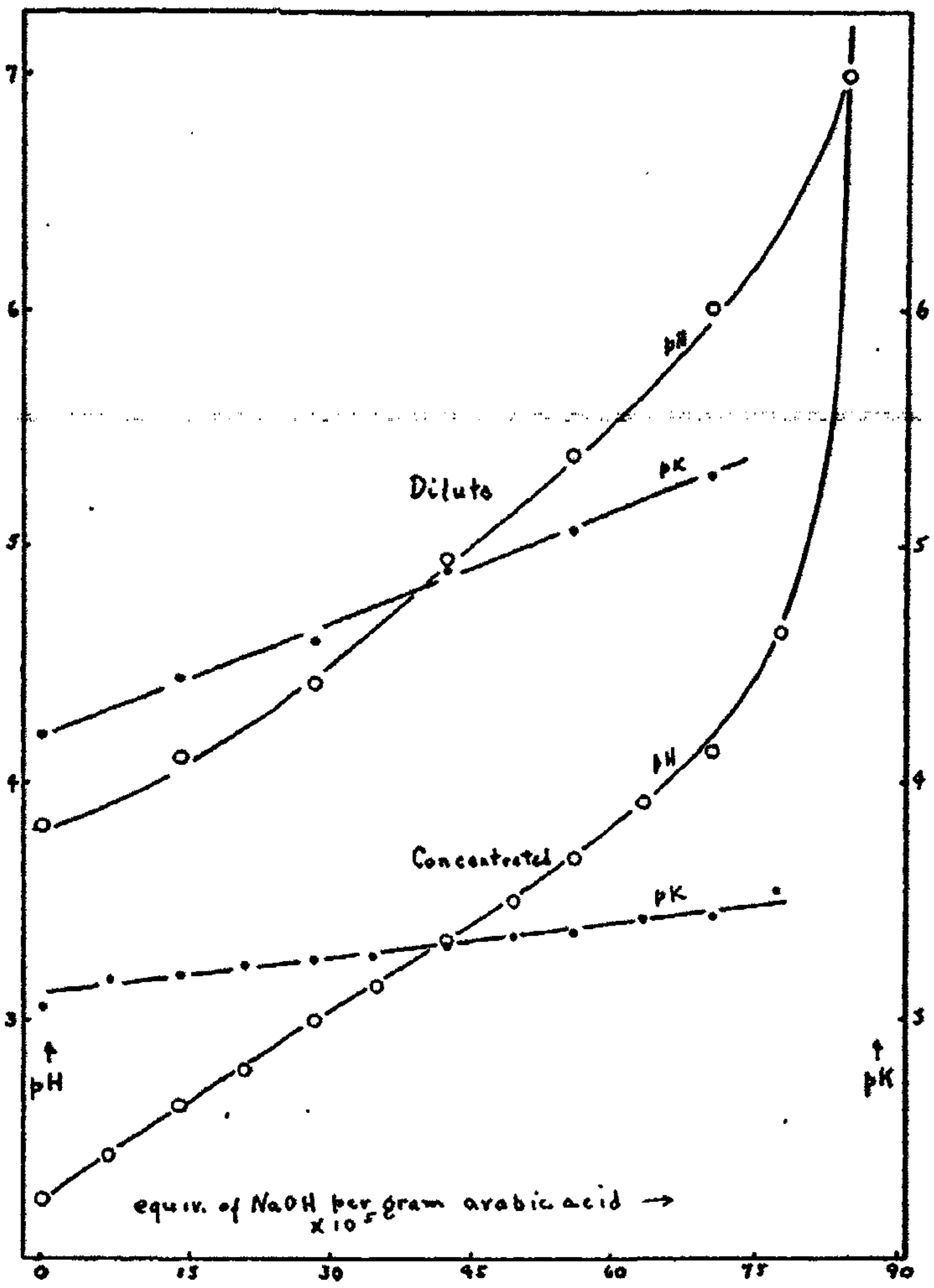

FIG. 3. TITRATION CURVES OF ARABIC ACID AT THE TWO CONCENTRATIONS, 50 G. AND 0.625 G., RESPECTIVELY, OF THE ACID IN 1000 G. OF WATER, AND THE VARIATION IN THE CALCULATED VALUES OF THE DISSOCIATION "CONSTANT" (K) OF THE ACID (PLOTTED AS pK) WITH THE DEGREE OF NEUTRALIZATION

continuously. This must mean that the acid is acting more and more like a very weak acid as the dilution increases. This conclusion is substantiated by the fact that the degree of ionization of the acid reaches a maximum and rapidly falls off with increased dilution. The observed α curve is the resultant of two tendencies: the one, the increased ionization with dilution, i.e., that commonly observed with solutions of all but the very strong acids; the other, the decrease in the dissociation constant of the acid with increased dilution, i.e., its tendency to dissociate decreases as it acts more and more as a very weak acid. The first factor predominates at the higher concentrations, and not until the rate of change in pK is very high (i.e., at highest dilution) does this factor predominate in the determination of the course of the α curve.

From the titration curves, the value of pK was calculated in a manner similar to that given above. Here, however, the sodium salt formed was considered to be completely ionized and $[A^-]$ was taken to equal $[H^+] + [Na^+]$, where $[H^+]$ was measured electrometrically and $[Na^+]$ was calculated from the amount of sodium hydroxide added. [HA] then would equal $[T] - [A^-]$. Figure 3 shows the titration curve and calculated pK values for the acid at two concentrations, one at a concentration of 50 mg. of acid per 1000 g. of water and the other at a concentration of 0.625 g. of acid per 1000 g. of water. These measurements were made upon solutions prepared by adding the desired amount of sodium hydroxide to solutions containing equal amounts of acid and then diluting the resulting solutions to contain equal weights of water. Thus there was no change in weight of solvent throughout the titration curve shown, and the varying pK calculated cannot be due to the dilution factor shown to exist in the above experiment with the acid.

Both of these titration curves show the acid to be completely neutralized at pH = 7. In both cases the calculated pK increases as neutrality is approached. At the higher concentration this drift in pK is not so great as at the lower concentration. And, in accordance with the dilution data on the acid, the value of pK increases with dilution. This shift of the pK value with neutralization may be taken to indicate that the latter of the above-mentioned pictures of the dissociation tendencies of the acid groups is more nearly the correct one. As alkali is added to the acid, the acid groups showing the greater dissociation tendency are first neutralized, and the average dissociation "constant" of the remaining acid groups is of a lower order of magnitude than before this fraction of the acid hydrogen was replaced by alkali cations.

Two conclusions to be drawn from these data on the apparent dissociation constant of the acid are: first, the various acid groups present have dissociation constants which are distributed in a continuous manner over the buffer range of the acid in such a way as to give a titration curve which resembles that of a monobasic acid in that there is only one definite buffer range; and second, the average dissociation constant for all these groups decreases at a continuously increasing rate with dilution.

This latter conclusion may be taken to indicate a readily reversible change in the size of the micella accompanied by a shift in the tendency toward ionization of the acid groups on the micella.

An analogous situation is found in the case of silicon dioxide sols. Rabinowitch and Laskin (4), from measurements of the electrical conductivity and potentiometric titration curves for an electrodialyzed solution, found a value of the dissociation constant of colloidal silicon dioxide equal to $K_1 = 2 \cdot 10^{-4}$. Their titration curves showed the solution to have a buffer region at pH 3 to 5. Willstätter and coworkers (6) prepared silicic acid solutions by hydrolysis of silicon tetrachloride in water in presence of silver oxide and obtained an acid which, immediately after preparation, showed a freezing point depression which indicated it to be molecularly dispersed. They found that polymerization immediately set in and proceeded at a more or less rapid rate thereafter, finally resulting in a colloidal solution of polysilicic acid of uncertain composition. They made potentiometric titration curves on their freshly prepared acid and upon the same after several days. They found a buffer region for the fresh solution at about a pH of 6.5, which shifted to lower pH as polymerization proceeded. The calculated value of the dissociation constant for their freshly prepared acid (i.e., pK is taken to equal the pH of half-neutralization in the buffer region of the acid) is found to be $K_1 = 5 \times 10^{-7}$.

Hogg (1) determined the value for the dissociation constant of true dissolved silicic acid from the degree of hydrolysis of sodium silicate solutions and found $K_1 = 10^{-9}$ and $K_2 = 10^{-13}$.

All this work seems to indicate that the greater the degree of polymerization of the silicic acid, the greater becomes the value of the dissociation constant and the strength of the acid. If we can assume a reversible polymerization of the arabic acid with increasing concentration, it is possible that the shift in the average dissociation constant of the acid may result from this in a manner similar to that observed with silicic acid solutions. One marked difference between these two colloids is that polymerization of the silicic acid solution is accompanied by dehydration of a part of the acid, while there is no indication that the number of readily reacting acid groups in the arabic acid changes with concentration (or, presumably, dispersion and polymerization).

SUMMARY

1. Equivalent conductivity values for arabic acid show a maximum at a concentration of approximately 0.00025 equivalent per liter. A maximum in the degree of ionization occurs at the same concentration.

Equivalent conductivity values for the potassium, sodium, lithium, and

calcium salts and for the ionized acid (i.e., calculated on basis of hydrogen-ion determinations) all show a minimum at a concentration of 0.0025 equivalent per liter. The prominence of this minimum varies to a degree which is roughly proportional to the ordinarily used mobility values of the cations employed, and totally disappears from the equivalent conductivity–equivalent volume curve for the strychnine salt of the acid.

It is postulated that the observed variation in the Λ–concentration curves is due to a change in the absolute mobility of the cations with concentration (the anion mobility being comparatively low) in accordance with the conclusions of Lewis concerning the variability with concentration of the transfer number for ions in ordinary electrolyte solutions, which also state that the effect is more marked when the mobilities of the two ions of the salt are markedly different.

It is to be concluded that the ionic activities of the cations present in these colloid electrolyte solutions will be different if measured electrometrically (as with the hydrogen-ion electrode) and if measured conductimetrically (assuming constant mobility of the ions), the degree of difference varying with concentration.

2. The titration curve for arabic acid shows only one buffer range. However it does not act as a monobasic acid, but as one the acid groups of which have varying ionization constants which are rather uniformly distributed throughout the buffer range of the acid. Calculated dissociation constants of the acid (regarding it as monobasic) give the average dissociation constant of all the acid groups present in the acid.

At any given concentration of the acid the dissociation "constant" decreases with the percentage neutralization, indicating that those groups of high dissociation constant are the first neutralized by added base and that this leaves the average dissociation constant of the remaining (unneutralized) groups at a lower value.

The dissociation "constant" of the acid decreases rapidly with increased dilution from a value of about $K = 1 \times 10^{-3}$ for a concentration of 50 to 100 g. of the acid per 1000 g. of water to near $K = 2 \times 10^{-7}$ at infinite dilution (extrapolation value). It is assumed that reversible peptization of the micella occurs when the solution is diluted and that this is accompanied by a marked decrease in the dissociation tendency of the acid groups present on the micella. Only in concentrated solutions does the acid act as fairly strong acid, though in all cases except, perhaps, in extremely dilute solutions the acid is completely neutralized at a pH of 7.

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THE OPTICAL ACTIVITY OF CAMPHOR IN ALCOHOLIC SOLUTIONS

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Received November 9, 1933

During the course of an investigation of the different methods used for the determination of camphor in spirits of camphor, it was necessary to prepare a large number of alcoholic solutions of camphor. These solutions were read in the polariscope and the specific rotations were calculated. Camphor is one of a number of organic substances which give different values for specific rotation when different strengths of alcohol are used as solvents. The rotation varies also for different amounts of camphor in the same percentage strength of alcohol.

One may find a number of references in the literature which give the specific rotations of camphor in ethyl alcohol. Among these may be mentioned Landolt (3), Moreau (5), Kazay (2), Malosse (4), Peacock (7), Francois and Luce (1), and Owen (6). However, no comprehensive study in which both factors (percentage camphor and strength of alcohol) are varied has been reported for the complete series of alcoholic solutions of camphor.

The samples of camphor used were the purest refined products which could be obtained on the market. The camphor was resublimed at least once; the first ten per cent coming over as sublimate was discarded, as was the last ten per cent remaining in the distilling flask. Pure ethyl alcohol which had been distilled over quicklime was used to make up the various dilutions of alcohol.

The camphor solutions varied in strength from 1 per cent to the highest concentration which the particular strength of alcohol used would dissolve. All solutions were made with the greatest accuracy and at the uniform temperature of 20°C. The solutions in each case were weight to volume solutions. Ten readings for each of the solutions were made in the polariscope at 20°C. The specific rotation was calculated by use of the formula

$$\text{Specific rotation} = \frac{\frac{a}{2.8835} \times 100}{l \times c}$$

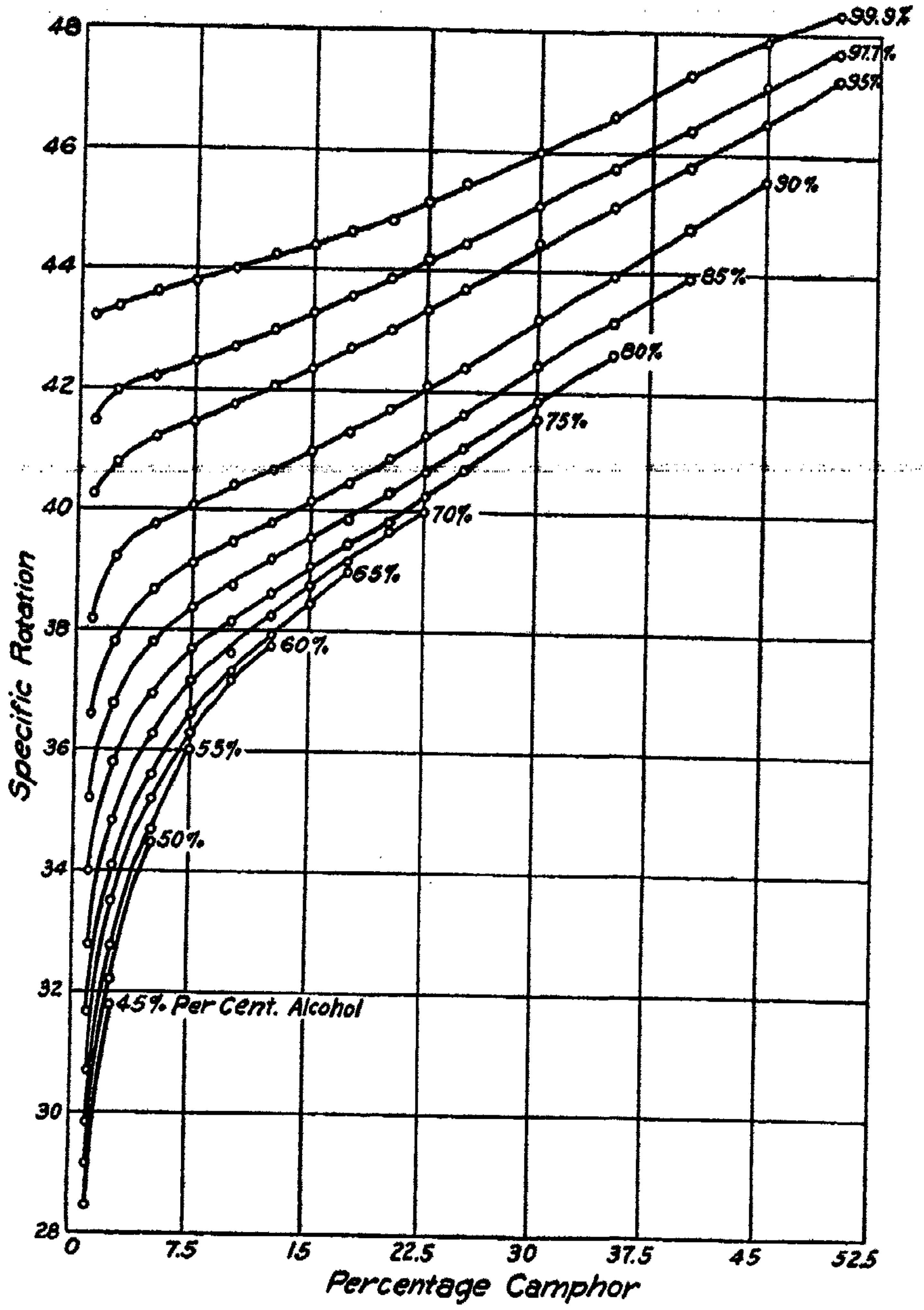

FIG. 1. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

where a is the polariscope reading, l is the length of the tube in decimeters and c is the concentration in grams per 100 cc. of solution.

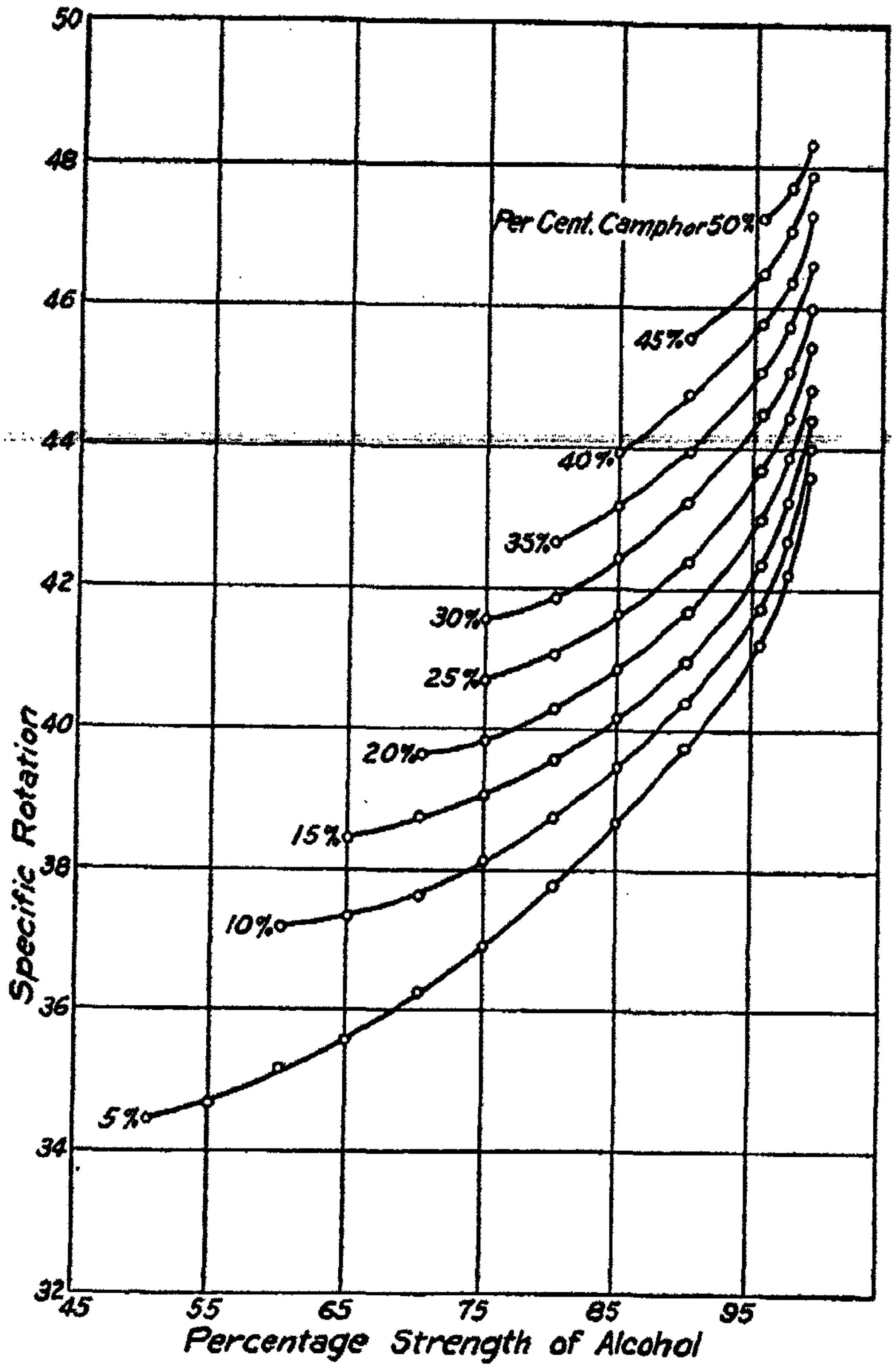

FIG. 2. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

The results are shown graphically in figures 1, 2, and 3. Figure 1 shows the curves obtained when the specific rotation is plotted against the percentage camphor. Figures 2 and 3 give the curves obtained when specific

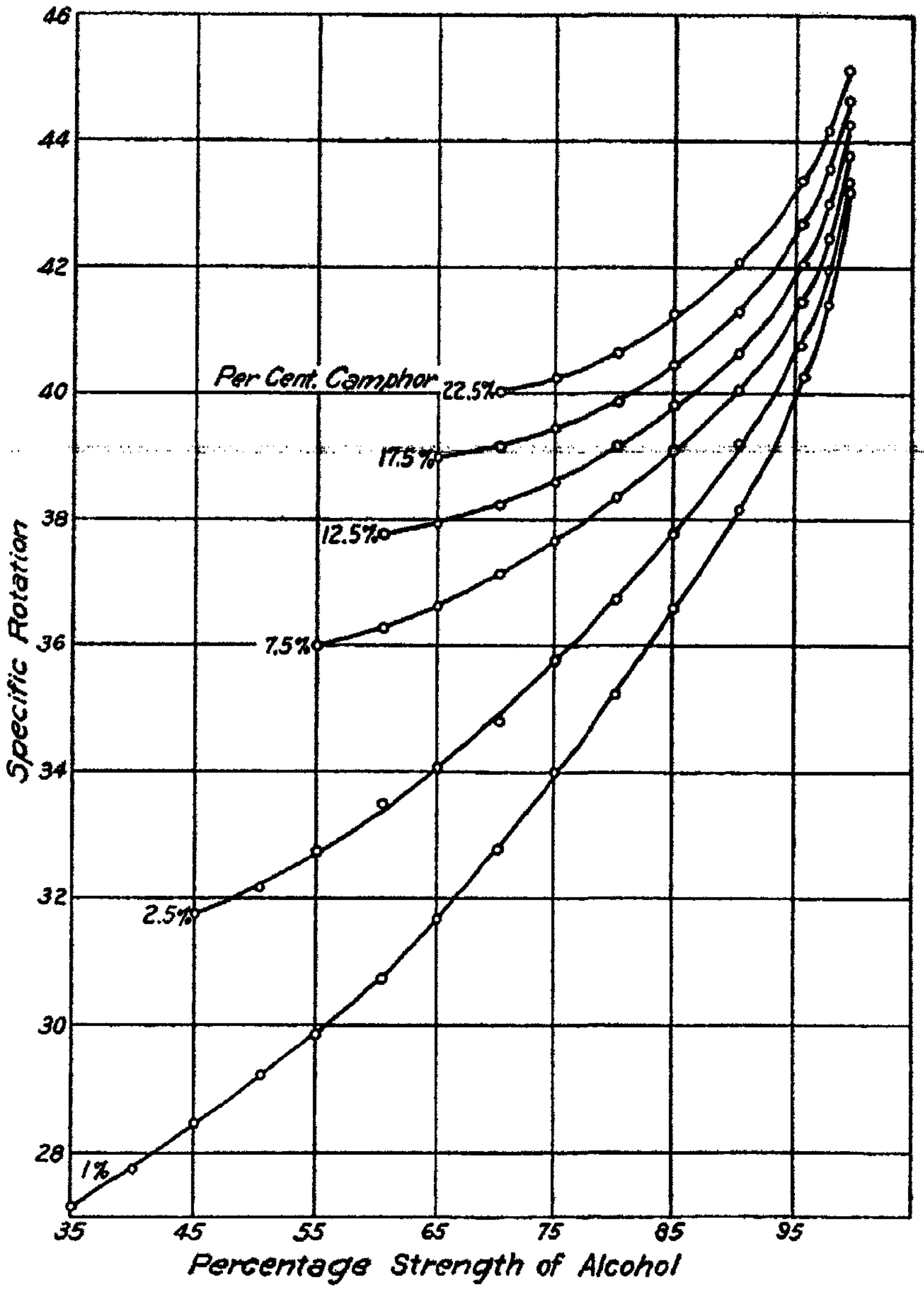

FIG. 3. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

rotation and percentage strength of alcohol are the variable factors. The curves given in these figures offer a practical means of determining an unknown factor when two of the three values—specific rotation, amount of camphor, strength of alcohol—are known.

From the figures we may see that the specific rotation varies considerably with a change in the strength of alcohol or with a change in the percentage of camphor dissolved. The values increase as the strength of alcohol increases. The specific rotation when the camphor content is 1 per cent varies from 27.14 for 35 per cent alcohol up to 43.18 for absolute alcohol. In the same strength alcohol the specific rotation increases as the amount of camphor dissolved increases. For instance, in 95 per cent alcohol the specific rotation varies from 40.24 for 1 per cent camphor up to 47.26 for 50 per cent camphor.

SUMMARY

1. The specific rotations for alcoholic solutions of camphor have been determined when the percentages of alcohol and camphor are varied over wide limits.

2. Curves have been constructed for determining a third factor when the values of two factors are known.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XIII

Chain Reactions in the Oxidation of Hydrogen in the Positive Column

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Received May 10, 1934

In a previous article on the oxidation of hydrogen in the glow discharge (4) it was shown that the explosive mixture could not be ignited in the negative glow, although ignition took place with ease in the positive column. The present research was undertaken, therefore, to contrast the reactivity in these two regions of the discharge, in the hope that it might throw some light on the factors determining propagation and on chain reactions in general.

APPARATUS

The discharge tube was a 5-liter Pyrex flask placed in an electric furnace which could be heated to 500°C. The cathode was an aluminum disc 3.2 cm. in diameter located at the bottom of the flask; the disc was encased in glass except for the top surface. The anode was an iron rod supported by a winch mounted on the neck of the flask that extended out of the top of the furnace; the position of the anode could be adjusted at will. The anode was 0.5 cm. in diameter and was encased in glass except at the lower end. The pressure in the system was read with a dibutyl phthalate manometer. The gases used were prepared in the manner described previously.

The rate of reaction was determined from the change in pressure per unit time. The rate in the positive column was obtained by subtracting the rate in the negative glow from the over-all rate. Unless otherwise stated all data were taken at room temperature.

RESULTS

The effect of pressure

The effect of pressure on the rate of reaction in a 2-cm. length of positive column is shown in figure 1. The discharge current was 10 ma.

Curve I is the observed rate, curve II the voltage, and curve III the volts required to synthesize one molecule of water. The values given are for the initial rates. The pressure vs. time curves from which the rates were obtained show the rate to be about constant for the first few minutes of each run, and then to decrease slowly with time.

A comparison of curves I and II shows that the rate increases more rapidly than the voltage, especially at the higher pressures. In consequence the power consumed per water molecule formed is nearly constant at the lower pressures, but decreases appreciably as the pressure is increased.

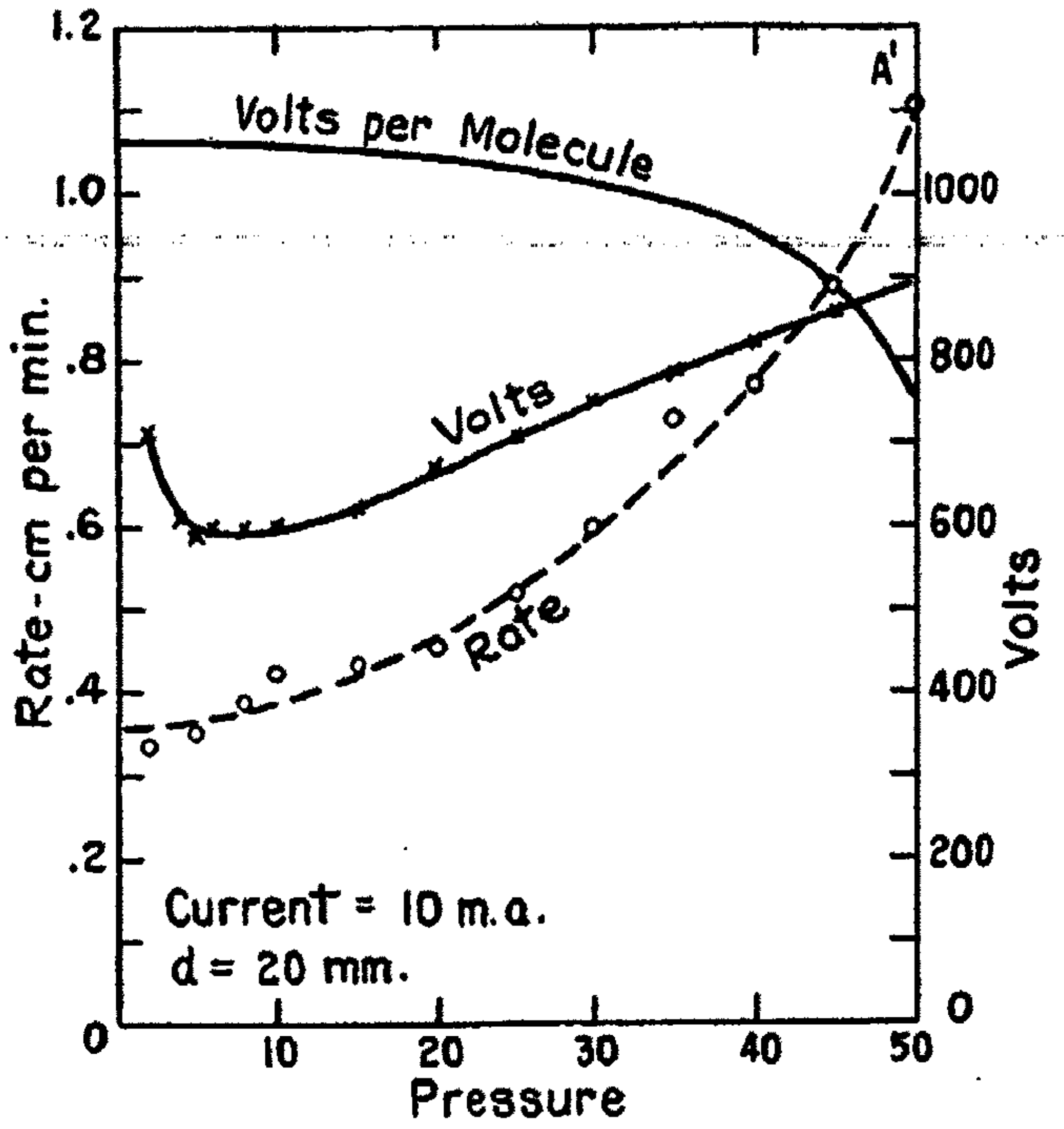

FIG. 1. THE EFFECT OF PRESSURE ON THE REACTION RATE

These results are in distinct contrast with those obtained previously in the negative glow, where the rate was shown to increase only very slightly with the pressure.

The effect of the current

The effect of the current on the rate is shown in figure 2.

The electrode separation was 47 mm. for the positive column and 3 mm. for the negative glow. The potential drop between the electrodes was 650 and 375 volts, respectively.

The data show the rate of reaction in the positive column to be proportional to the current below 25 ma. at the pressures used; above this point the rate increased, and the power expended in terms of volts per molecule dropped rapidly to a very small value.

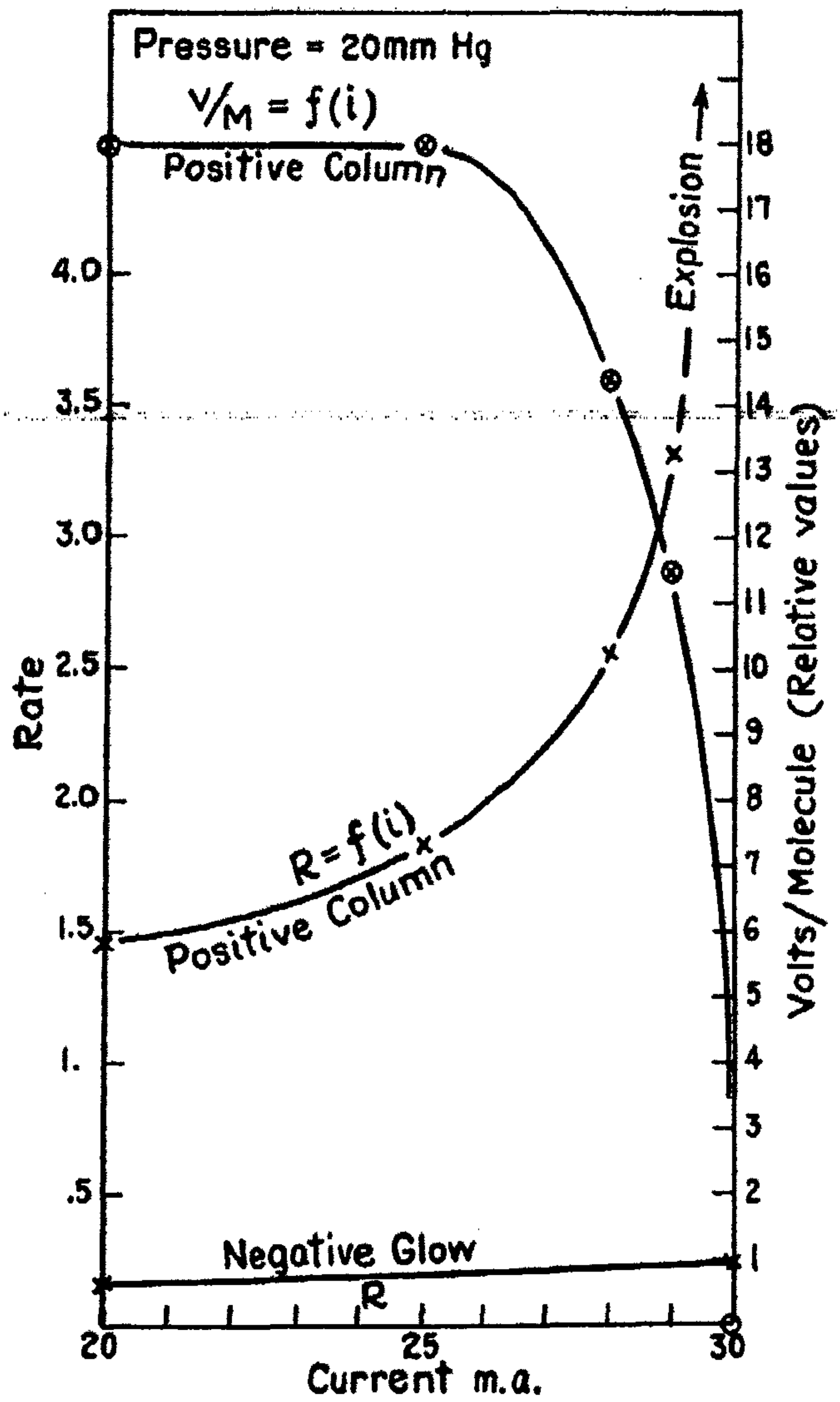

FIG. 2. THE EFFECT OF CURRENT ON THE REACTION RATE

These results are again in contrast with those in the negative glow where the rate was found to be proportional to the current over the range investigated.

The effect of voltage

In the cases where the change in the discharge voltage varied with the current the rate of reaction (R) was proportional to the power input rather than to the current. This is shown in table 1. These results were taken at a pressure of 2.3 cm. of mercury and with an electrode separation of 4.7 cm.

The effect of added gases

The effect of the addition of 3.1 mm. of gas to 18.5 mm. of explosive mixture on the reaction rate is given in table 2. M refers to molecules synthesised, e to electrons, and V to volts. The length of the positive column was 7 mm. and the current was 25 ma. The tests were made with a low per cent of added gas in order that the fraction of energy absorbed by this gas should be low.

TABLE 1

i	V	R	R/i	$R/iV \times 10^3$
8	490	10.80	1.35	2.76
10	442	11.56	1.16	2.63
12	408	13.00	1.08	2.65
15	372	15.38	1.02	2.75

TABLE 2

The effect of added gases on the reaction rate

ADDED GAS	M/e	V/e	V/M
None	20.2	100	5.0
Hydrogen	20.4	105	5.1
Oxygen	33.4	70	2.1
Nitrogen	21.3	85	4.0
Argon	18.2	70	3.8
Helium	17.3	75	4.9

In the negative glow the rate was proportional to the partial pressure of hydrogen up to 90 per cent added gas, helium had no effect, and nitrogen, oxygen, and argon had a retarding action in the order named.

The effect of various amounts of added gas is shown for argon in figure 3. The difference in the effect of added argon on the reactivity in the two regions of the discharge is very pronounced. In the negative glow argon decreases the rate in a manner very nearly proportional to the amount present. Just the opposite condition exists in the positive column, where the rate increases linearly with the partial pressure of the argon up to 50 per cent added gas.

The effect of water vapor on the reaction rate is shown in figure 4. These curves were obtained from the tangents at different points along the time vs. pressure curves. No correction was made for the change in pressure during the course of the run, since the total pressure used was such that the pressure coefficient was small. The dotted portion of the curve represents an extrapolation, made necessary by the fact that the time vs. pressure curves for the currents used showed a small heating effect at the beginning of the run; the extrapolation, therefore, was made from data obtained when the discharge current was 5 ma.

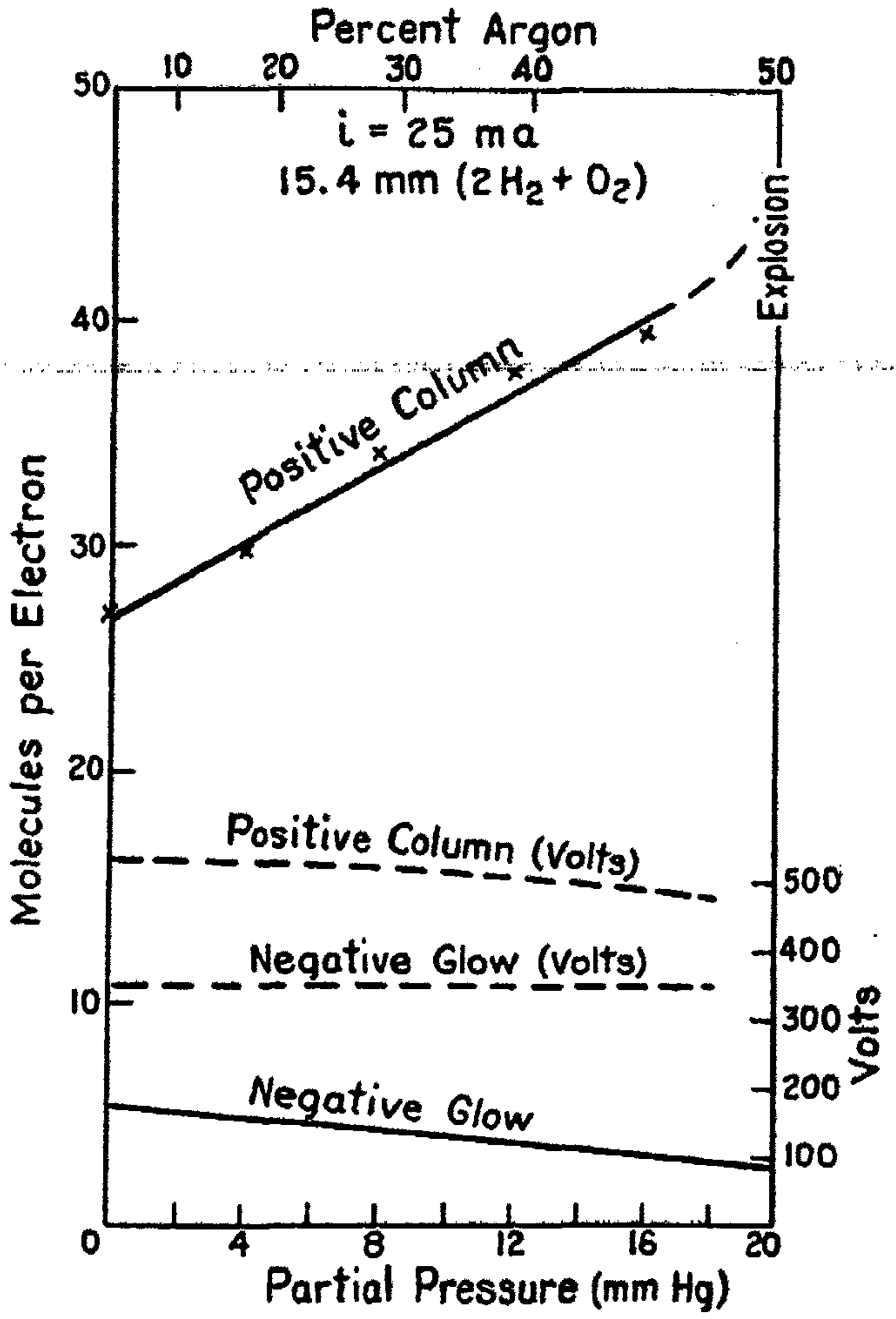

FIG. 3. THE EFFECT OF VARIOUS AMOUNTS OF ARGON ON THE REACTION RATE

It will be observed that up to 40 per cent water vapor the rate is the same as in the 2:1 mixture for both the negative glow and the positive column. In this respect its behavior is distinctly different from that of argon. The fact that the rate in the negative glow is unchanged by the addition of water vapor is an indication that water molecules also can furnish reaction nuclei. Substantially the same result has been obtained by Lind and Schiflett using alpha rays (9).

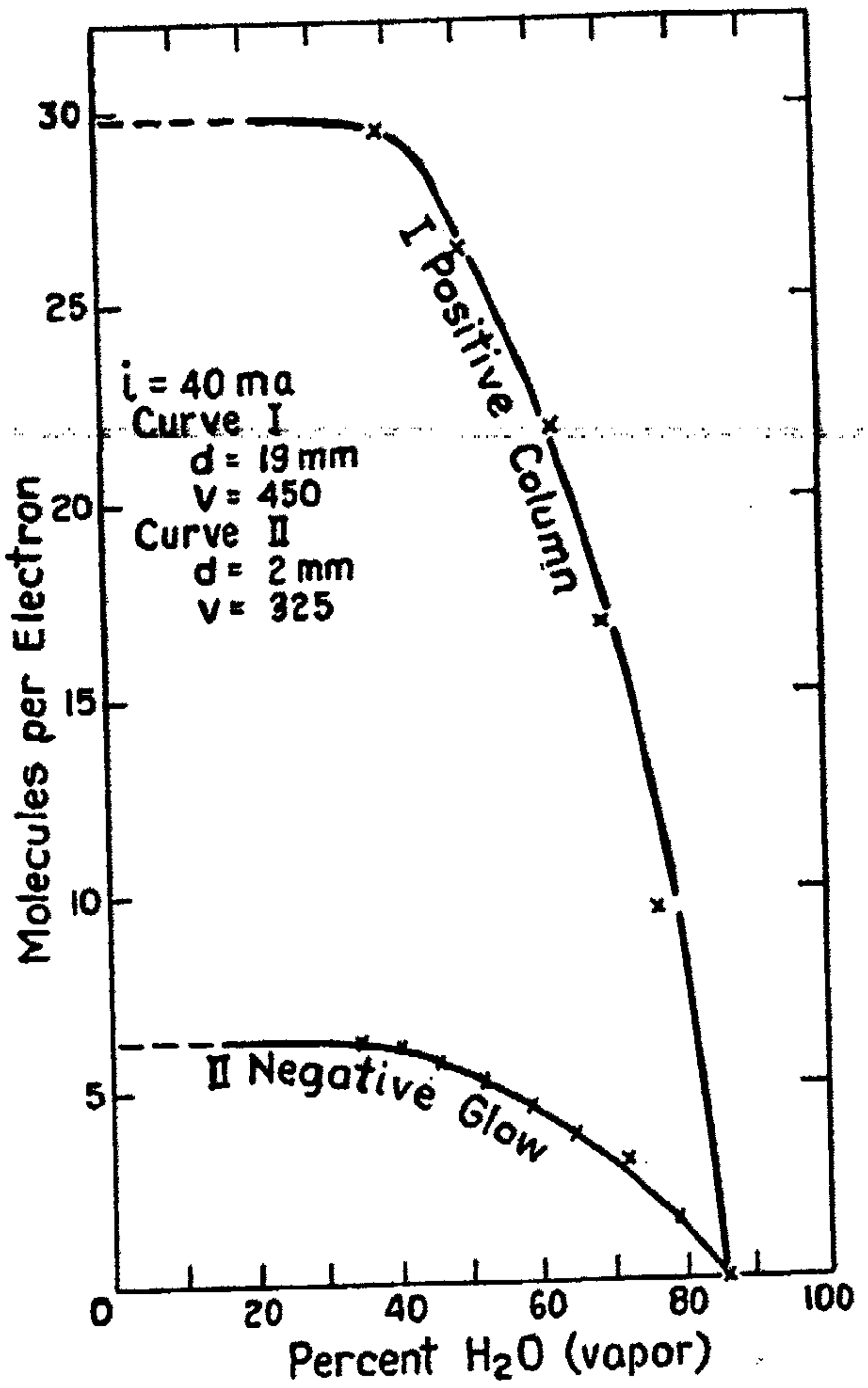

Fig. 4. The Effect of Water Vapor on the Reaction Rate

It is interesting to note that the water vapor–$2H_2:O_2$ equilibrium occurs at about 88 per cent water for both regions of the discharge.

The effect of the walls

The effect of the proximity of glass surfaces on the rate was determined by surrounding a discharge between two aluminum rods—3 mm. in diameter, 5 mm. in exposed length, and 2 cm. apart—with glass cases of different sizes. In table 3 are given the results obtained with two such cases. The cylinder was a tube 2.7 cm. long and 3.2 cm. in diameter placed symmetrically over the discharge, the axis of the cylinder being perpendicular to the path of the discharge. The case was 1 cm. on the end, 3.8 cm. on the side, and 2.7 cm. long and was similarly placed.

The values given are for the over-all reaction. M/e is molecules per electron, and V/M is volts per molecule.

The data show that the reactivity probably approaches the same rate for low currents. As the current is increased, the retarding effect exerted by the close proximity of surfaces becomes more and more pronounced. Since both cases were placed to permit unimpaired convection through the discharge, the retarding action at the higher currents must be due to limitations in the reaction chains, as is evidenced by the fact that the gas could not be ignited in the rectangular case, while the cylinder had little effect on the ignition energy.

TABLE 3

CURRENT	GLASS CYLINDER		GLASS CASE	
	M/e	V/M	M/e	V/M
20	37.1	13.8	31.5	18.1
25	36.9	13.8	30.5	18.7
30	39.9	12.8	28.0	20.0
35	49.1	10.4	24.7	22.3
38	55.6	9.5		
40	Ignition		22.9	24.0

The effect of temperature

In the negative glow the rate of reaction exhibited no temperature coefficient for low current densities and only a detectable positive coefficient for the higher currents. In the positive column the coefficient was more positive, the rate increasing about eightfold for a 300°C. rise in temperature. The effect of temperature is dependent on the conditions existing in the discharge, being influenced by both current and pressure.

DISCUSSION OF RESULTS

A survey of the differences in the reactivity in the negative glow (4) and in the positive column when correlated with the physics of these two regions may be of some help in understanding the mechanism of reaction involved. In the negative glow evidence was advanced to show that the reaction took place largely about H_2^+ ions and that in comparison O_2^+ ions, atoms, and excited molecules were relatively poor reaction centers. It was shown further that most of the water synthesized reached the walls carrying a positive charge in the negative glow, and as neutral molecules in the positive column.

The difference in the reactivity in the two regions of the discharge is distinct. In the negative glow the M/N ratio is nearly constant, being independent of the pressure and the current density. In the positive column the M/N ratio increases with both the power input and the pressure, due definitely to the presence of reaction chains which are completely absent in the negative glow.

Two alternatives are possible in interpreting the above results. Either some condition is to be found in the positive column that permits the H_2^+ ions to have an M/N ratio far higher than the fixed ratio in the negative glow, or else new active centers come into play that are capable of serving as chain heads.

The physics in the two regions of the discharge differs primarily in the energy of the electrons. In the negative glow measurements of the range of the electrons show that the initial energy corresponds to the entire cathode fall in potential, being of the order of several hundred volts. This energy is dissipated largely in the production of ions (one ion for about 45 volts (5)) and in the excitation of both low and high quantum states. The values of Lehman fix the ratio of $M/H_2^+ = 2$, which is probably more accurate than the value 4 given in the previous communication. A line as well as a band spectrum is emitted. In the positive column, the average energy of the electrons is about 4 or 5 volts, while the maximum energy only slightly exceeds the ionization potential of the gas. The energy is expended largely in the production of ions and in the excitation primarily of lower levels in a large number of molecules. The spectrum ordinarily consists of bands.

It is very improbable that any excited state capable of initiating a chain can be found that exists only in the positive column; ions are abundant in both regions, while atoms and excited molecules, especially those of high energy content, are more prevalent in the negative glow. The expenditure of energy per unit volume of the discharge may be some twenty times greater in the negative glow than in the positive column, as can be seen from figure 4. Roughly the concentration of most excited states will be in proportion to the power expended. In the case of neutral atoms, however, the concentration should be even more pronounced in the negative glow, since they are not produced by direct electron impact but largely, if not entirely, by the dissociation of the excited ions which are present in appreciable quantities only in the negative glow. The ions formed in the positive column of the direct current low density discharge of the type used are of the normal variety, and hence do not dissociate appreciably.

Since it does not seem possible to find new reactive states existing only in the positive column, one is naturally forced to the other alternative that for some reason chains are set up by the original reaction centers in this region of the discharge, while they are not set up in the negative glow. Chain mechanisms seem limited to three general types: (1) atom chains, (2) excited molecule chains, and (3) cluster chains. A brief consideration of each of these may show the one most capable of explaining the observed facts.

Bonhoeffer and Haber (1) suggest a chain starting with H and continuing consecutively through H and OH. Obviously such a chain should start in the negative glow, where the concentration of H atoms is the highest. The fact that the *M/N* ratio is constant in this region necessarily eliminates this type of atom chain.

Thompson and Hinshelwood (11) postulate a chain the principal links of which are hydrogen peroxide and activated water molecules. While the mechanism is somewhat indefinite, it is again impossible to see how this type of mechanism could account for the entire reactivity in the discharge without being more pronounced in the negative glow than in the positive column.

In view of what has just been said it does not seem probable that the usual types of chains involving atoms and excited molecules can be used to account for the observed conditions. A modification of the cluster mechanism originally formulated by S. C. Lind offers some prospects of success. The basis of the Lind mechanism, devised for alpha-ray ionization, is that the reaction results from the neutralization of a positive ion or cluster by a negative ion or cluster. Since the postulated reaction does not take place until neutralization occurs, the *M/N* ratio is limited by the size of the clusters at this instant; obviously, therefore, the ion cannot serve as a chain head. In applying the cluster mechanism to the glow discharge it was necessary to modify the original Lind concept, since neutralization takes place largely at the walls and not in the gas phase as with alpha rays. It was suggested (3), in consequence, that the reaction occurs between just those molecules closely associated about the positive ions, and that the reactivity ceases upon neutralization. The ions, therefore, can serve as reaction centers until neutralized, and hence high *M/N* ratios or ionic chains are possible. Since the water molecules synthesized in the negative glow reached the walls carrying a positive charge, it is necessary to make the further assumption that reaction does not occur between the molecules associated about the ions until the clusters receive energy from the outside equal to their energies of activation; this may come from collisions with "hot molecules" or from the heat of neutralization by electrons. This type of mechanism will satisfy the demands imposed by the discharge.

The conspicuous difference in the conditions influencing the possible active states in the negative glow and in the positive column appears to be in the length of life of the ions in the gas phase. In the negative glow the ions are driven rapidly to the wall, so that the chance of the ion being struck by an electron or molecule of high energy content is far smaller than in the positive column. The ion, therefore, carries its original cluster to the walls, and the reaction is confined to just those molecules associated about it. In the positive column the life of the ion in the gas phase being longer, its chance of being struck by a body rich in energy is correspondingly large. If this colliding body possesses an amount of energy E sufficient to cause the molecules associated with the ion to react, the total energy of the associate will be $(E + Q)$, where Q is the heat of formation of molecules synthesized. This energy, when Q is large as in the present case, will be sufficient to disrupt the cluster, leaving the ion denuded of its associated molecules; the ion (not necessarily in the original form) is then in a condition to start the process all over. The only difference is that the ion after the disruption of the cluster doubtless contains some fraction ϕ of the energy $(E + Q)$; hence the energy of activation for the new associate will be not E but $E - \phi$. The water thus formed will be liberated in the gas phase largely as neutral molecules.

A typical ionic chain reaction can be illustrated graphically by the following equation:

$$\underbrace{\underbrace{H_2^+ \xrightarrow{H_2 + O_2} [H_4O_2]^+}_{\text{Negative glow}} + E \longrightarrow \underset{\hookrightarrow H_2O}{[H_2O]^+} \xrightarrow{H_2 + O_2} [H_4O_3]^+ + E \longrightarrow \underset{\hookrightarrow H_2O}{[H_2O_2]^+}}_{\text{Positive column}} - - -$$

Since the water ejected from the cluster contains a large fraction of the energy $(E + Q)$, it can serve as a means of supplying energy E to another cluster.

It should be mentioned that an ionic chain of this type involves no difficulties arising from energy considerations; it is amenable to the general mathematical treatment given by Semenoff (10) for chain reactions; it requires no triple collisions; it accounts for the fact that flame fronts are strongly positively charged, as has been shown in a very ingenious manner by Lewis (6) or as may be seen by placing a flame in an electric field; likewise it accords with the very interesting observations of Lewis and Kreutz, wherein it was shown that flame temperatures are lowered by transverse electric fields (7), and that the ignition temperature of combustible gases is lowered by ionizing the gases previous to their admission to the ignition chamber (8).

On the basis of this mechanism the acceleration in rate of reaction observed in the positive column by oxygen, nitrogen, and argon is easily seen, as these gases, being much heavier than hydrogen, tend to slow down the rate of diffusion to the walls and hence increase the chance of the cluster being struck by an energy-rich molecule. The abnormally large effect of oxygen suggests that O_2^+ ion clusters may also serve as chain initiators provided the energy E of the colliding molecule is sufficiently high. A general extension of this mechanism can now be made to the effect that reaction may occur about any ion or polar molecule capable of associating itself with molecules when this associate is struck by a molecule containing an energy E, equal to or greater than that necessary for activation of the particular associate in question. Since the field of force about an ion or highly polarized molecule is essentially the same as that existing at conducting surfaces, the energy of activation (E) will have the same significance in both cases (2).

The hypothesis just advanced gives for the number of molecules synthesized per unit of current in the negative glow $m = M/N_{H_2^+} \times n$, where n is the number of H_2^+ ions formed, the number of reaction centers being given by $w = n$. This equation also applies in the positive column when propagation is not present; when propagation occurs, another term must be added to take account of the molecules formed in the chain. The probability that the ion will form more molecules than that given by the original M/N ratio depends on the chance of the associate colliding with molecules containing energy equal to $E - \phi$ or greater. Thus the probability of the ion continuing the chain is

$$a = e^{-\frac{E-\phi}{kT}}$$

where k is Boltzmann's constant. The effective number of reaction centers in the positive column, therefore, is given by

$$w = n + wa = \frac{n}{1-a}$$

If the heat of reaction is small or negative, ϕ will be small compared to E; then a will be small and the wa term will contribute little or nothing to the reaction. This is the case in the negative glow where there is little chance of the new formed water molecules adding their energy to other associates. An increase in Q, combined with the possibility of this energy being returned to a new associate, results in an increase in a with a corresponding contribution by the wa term. Thus when $a = 1$ the chain will be just self-supporting; when $a > 1$ not only will the chain support itself but new reaction centers will be formed in the process, giving rise to branching chains.

Reaction chains of the type just described may be broken in several different ways. The removal of the clustering centers from the sphere of reaction limits the length of the chain, as may be seen in the negative glow and in the proximity of walls. Lowering the energy density of the gas through which the chain head is moving will cause its reactivity to cease; this is shown by the action of added gases, by the non-proportionality between current and rate, and by the effect of temperature. The selective association of inert molecules about the reaction center may also cause the reactivity to cease. This is illustrated in figure 4 by the shortening of the chains as equilibrium is approached; the chains are broken apparently by the water molecules forming stable clusters with the active centers, thus preventing the association of hydrogen and oxygen.

SUMMARY

1. In contrast to a fixed ratio of $M/H_2^+ = 2$ in the negative glow, the rate in the positive column increases with both current and pressure until the ignition point is reached.

2. The rate of reaction is accelerated by added gases in accordance with their ability to retard diffusion, the effect being almost the opposite to that in the negative glow.

3. The rate is retarded by the presence of walls and accelerated by temperature.

4. The results are interpreted as indicating the presence of reaction chains in the positive column but not in the negative glow.

5. Reasons are advanced to show that the chains must be of the cluster type and cannot consist of atoms or radicals.

6. The mechanism, as well as the factors influencing the cluster type of chains, is discussed.

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THE SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER, METHANOL, AND ETHANOL

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Received December 28, 1933

INTRODUCTION

The solubility of ammonium thiocyanate in water at low temperatures has been determined by several investigators (3, 6, 9, 10). No previous determinations of the solubility of ammonium thiocyanate in methanol or in ethanol have been made. These data are of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

MATERIALS

The ammonium thiocyanate used was Baker's C.P. grade. The ammonium thiocyanate as received showed a melting point of 149.0°C., but as some solid insoluble materials were present, it was further purified by two recrystallizations from methanol according to Lunge (7), who states that the resulting product is non-hygroscopic. This was found to be the case. The melting point of the ammonium thiocyanate after the above treatment was 149.7°C., which agrees closely with the value 149.6°C. recorded in the literature (5).

It was found necessary to employ all glass or porcelain apparatus in every stage of the process and to avoid possible contact with iron in any form. Solid ammonium thiocyanate or its solution on contact with even an iron spatula gave a pink colored product, no doubt due to the formation of iron thiocyanate, $Fe(SCN)_3$. By using all glass or porcelain apparatus, the resulting recrystallized salt was absolutely white and free from color. It was further observed that when the ammonium thiocyanate was colored with ferric thiocyanate, and the product was heated at 60°C. for a period of hours, the color disappeared.

In addition to the melting point determination, the purity of the ammonium thiocyanate was checked by chemical analysis for its ammonia and thiocyanate content. The ammonia was determined by distillation (2) and showed an average of 22.40 per cent (three determinations) with a maximum deviation of 0.06 per cent. The slightly higher ammonia content than the theoretical may be due to the possible liberation of ammonia from the thiocyanate group as mentioned by Pfeiffer (8). The thiocyanate content was determined by Volhard's method (15) and showed an average of 76.29 per cent (three determinations) with a maximum deviation of 0.05 per cent.

The water, methanol, and ethanol used in the present research have been described previously (11).

PROCEDURE AND APPARATUS

The synthetic method of Alexejew (1) was employed in making the solubility determinations. The procedure and apparatus used in the present research have been described earlier (11, 12, 14).

Some preliminary data were obtained for the possible conversion of ammonium thiocyanate in water solutions. Samples were heated with water at 100°C. for two hours and then analyzed for ammonium thiocyanate. The ammonium thiocyanate solution when analyzed indicated practically 100 per cent ammonium thiocyanate. This indicated that the procedure had not affected the ammonium thiocyanate. In the determinations that follow the solubility temperatures were considerably lower than 100°C. and were always kept for less than two hours at their respective solubility temperatures. This preliminary data would indicate that no change in the nature of the solute had taken place during the solubility temperature determinations. These findings are in accordance with the results of Waddell (16), who showed that ammonium thiocyanate is very slowly if at all changed at temperatures below 110°C., whether heated alone or in aqueous solution.

It had been pointed out earlier (11) that precautions to insure the presence of small crystals are one of the means of obtaining true equilibrium conditions. An apparent anomaly to this criterion was found in the case of the ammonium thiocyanate–ethanol system. In this system fine crystals could be obtained without difficulty. However, the crystals were so fine as to give a colloidal turbid opalescent solution with the result that, when the ordinary procedure for solubility determinations was followed, the solubility temperatures were overstepped by one or more degrees. To overcome this difficulty, it was found necessary to cool the solution slowly so as to favor the formation of large crystals. Starting with large crystals and thermostating for a period of ten minutes, it was found that the true solubility temperature could be obtained.

EXPERIMENTAL RESULTS

The results of the various ammonium thiocyanate solubility determinations are presented in tables 1, 2, and 3. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data were plotted on a large scale according to the method of Hilde-

TABLE 1

Solubility of ammonium thiocyanate in water

(Recrystallized from methanol)

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
1.7853	1.2119	59.57	0.2588	13.00
1.8507	1.1247	62.20	0.2803	18.99
1.6550	0.8933	64.95	0.3043	26.33
1.9970	1.0319	65.93	0.3138	28.82
1.9798	0.8954	68.86	0.3435	36.36
2.3633	1.0105	70.05	0.3567	39.44
2.1629	0.8058	72.86	0.3885	46.92
2.5037	0.8557	74.53	0.4092	51.37
2.8356	0.9465	74.94	0.4154	52.50
2.2651	0.6909	76.63	0.4376	57.23
2.3848	0.6519	78.53	0.4637	62.46
2.2045	0.5451	80.18	0.4890	67.21
2.5536	0.5710	81.73	0.5145	71.53

TABLE 2

Solubility of ammonium thiocyanate in methanol

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
0.8746	1.4824	37.11	0.1989	24.58
1.0754	1.6099	40.05	0.2194	32.94
1.3375	1.6549	44.70	0.2538	44.80
0.9994	1.0279	49.30	0.2904	54.76
1.3020	1.0850	54.55	0.3356	64.55

TABLE 3

Solubility of ammonium thiocyanate in ethanol

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
0.3867	1.6416	19.07	0.1247	18.45
0.6283	2.2884	21.54	0.1421	33.25
0.6418	2.2545	22.16	0.1469	36.93
0.4571	1.4915	23.46	0.1565	43.36
0.6044	1.6572	26.72	0.1807	57.62
0.5958	1.4855	28.63	0.1953	64.20

brand and Jenks (4), as the log N_2 vs. $1000/T$. The solubilities at rounded temperatures were read off and are given in table 4.

DISCUSSION OF RESULTS

The results of the solubility determinations of ammonium thiocyanate in water were compared with those published by Rudorff (9, 10), Smitts and Kettner (13), Kettner (6), and Foote (3). This comparison is shown in graphic form in figure 1, where the data are plotted according to the method of Hildebrand and Jenks (4). It is felt that the foregoing results are accurate to well within ±0.10°C. of the true solubility temperature.

As shown in figure 1, the curve of the author's data is not a straight line function. If an attempt is made to extrapolate the curve to the point when the log N = 0, a value below the absolute melting point is obtained, indicating the ammonium thiocyanate does not form an ideal solution in water. Calculations from the vapor pressure data of Foote (3) also indicated that ammonium thiocyanate does not form an ideal solution in water.

TABLE 4

Solubility of ammonium thiocyanate in water and alcohols at rounded temperatures

(Expressed in mol fractions of ammonium thiocyanate)

TEMPERATURE	SOLUBILITY OF AMMONIUM THIOCYANATE IN		
	Water	Methanol	Ethanol
degrees C.			
20	0.2831	0.1886	0.1264
25	0.2999	0.1999	0.1322
30	0.3183	0.2119	0.1380
35	0.3381	0.2249	0.1443
40	0.3583	0.2388	0.1512
45	0.3803	0.2545	0.1591
50	0.4031	0.2719	0.1670
55	0.4266	0.2914	0.1757
60	0.4512	0.3136	0.1859
65	0.4764	0.3373	0.1972
70	0.5053	0.3631	0.2095

The solubility results of ammonium thiocyanate in methanol and ethanol are found in tables 2 and 3. These results are also presented in graphic form in figure 2. It is observed that in the temperature range studied, 20 to 70°C., ammonium thiocyanate in water, methanol, and ethanol does not form straight line functions when plotted as in figure 2. Furthermore, it is seen that ammonium thiocyanate is highly soluble in water, moderately soluble in methanol, and least soluble in ethanol.

When carrying out the solubility determinations of ammonium thiocy-

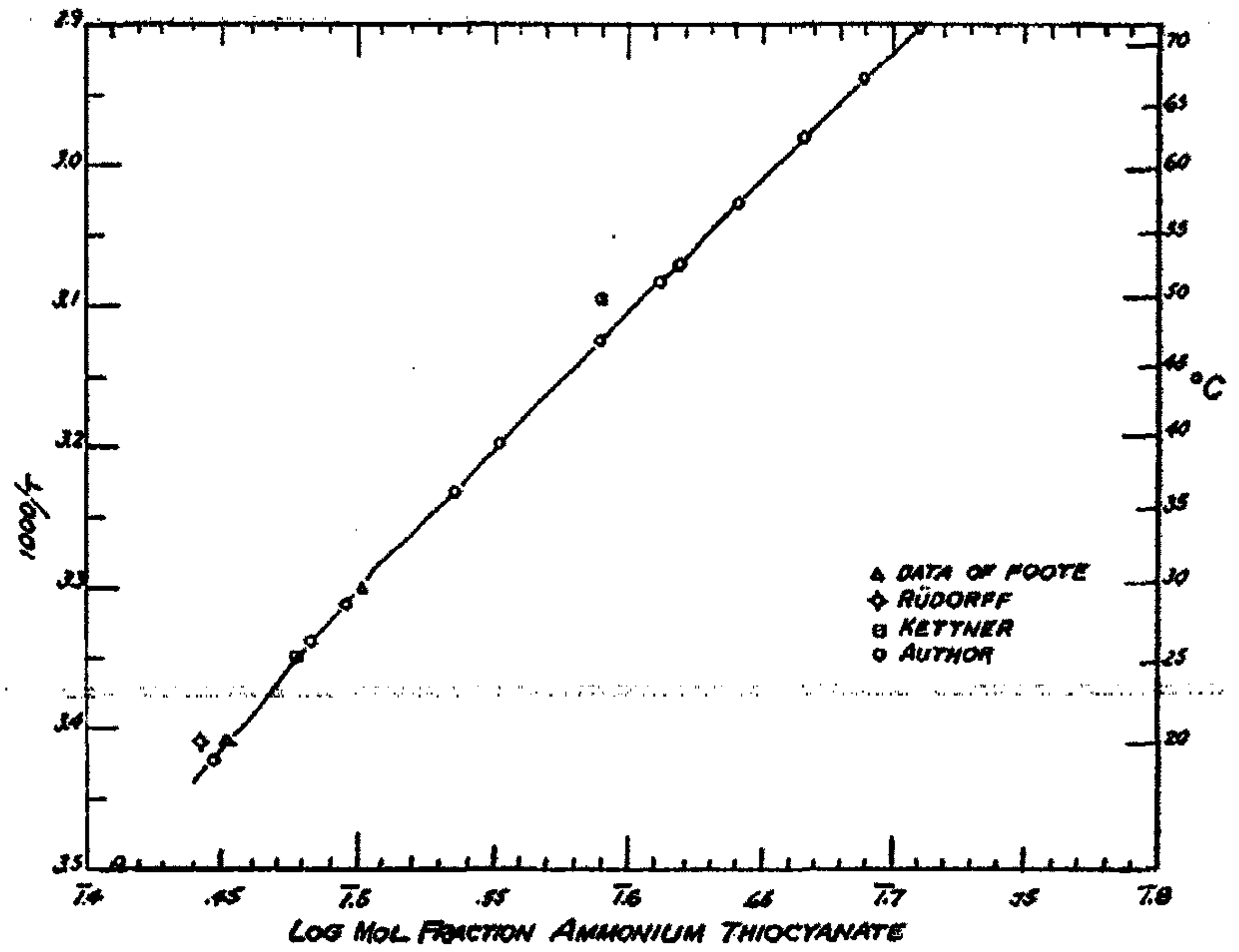

FIG. 1. SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER

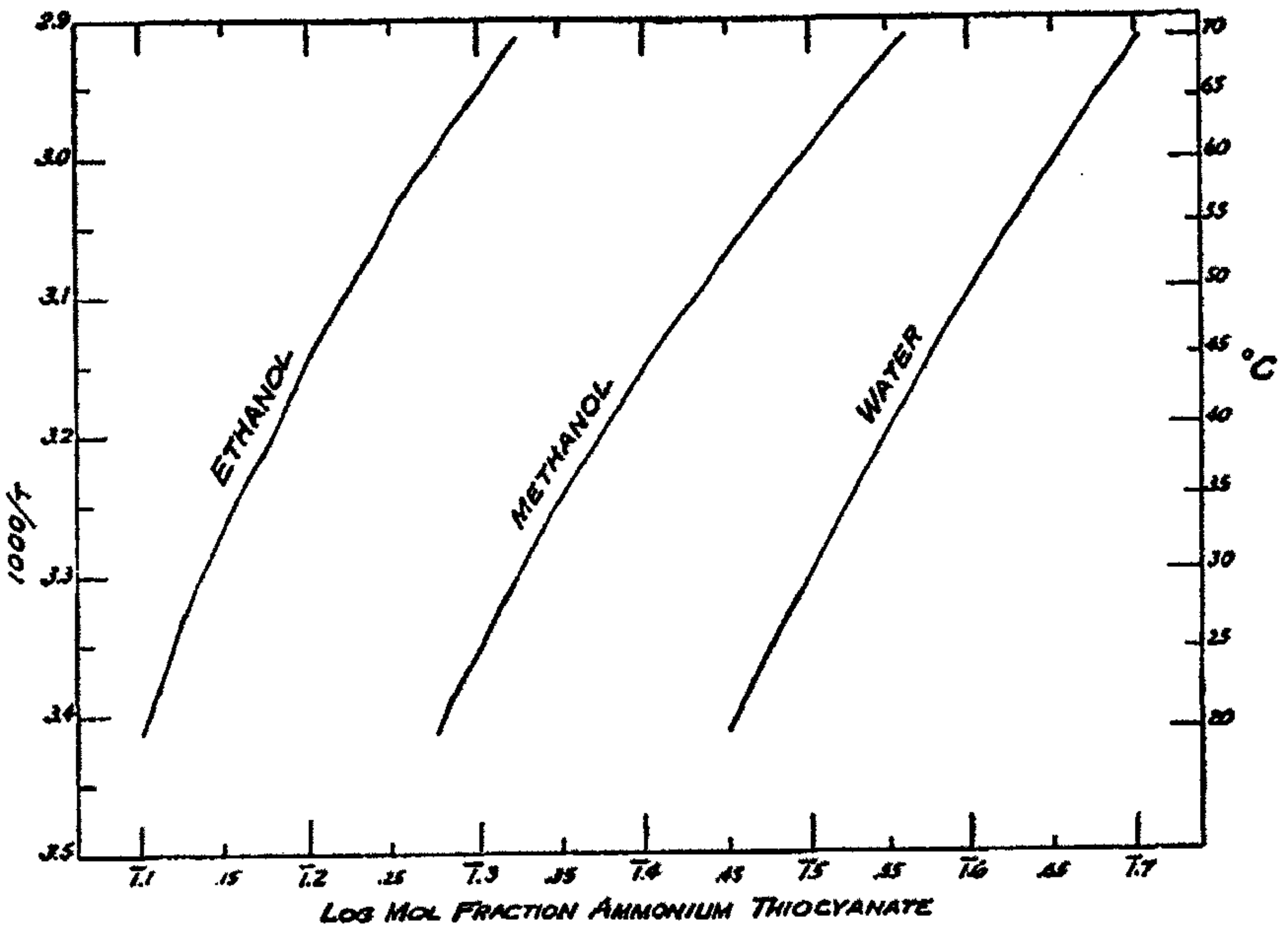

FIG. 2. SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER, IN METHANOL, AND IN ETHANOL

anate in ethanol, it was observed that the tubes as prepared at first were perfectly clear and colorless, but on standing and on exposure to light, in the heating period they turned yellow, and the yellow coloration increased with time. This observation would indicate that some change or reaction between the ammonium thiocyanate and ethyl alcohol was taking place.

SUMMARY

1. A sample of ammonium thiocyanate was carefully purified and analyzed.

2. Some thirteen determinations of the solubility of ammonium thiocyanate in water by the synthetic method in the temperature interval 13 to 72°C. have been made. The precision of measurement in these runs is higher than any previously published.

3. The solubility of ammonium thiocyanate in methanol and ethanol has been determined by the synthetic method from 20 to 70°C.

The author wishes to express his gratitude to Prof. A. A. Sunier for his interest and advice during the progress of this work, and to the Rochester Gas and Electric Corporation for the use of their equipment.

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LIESEGANG PHENOMENON IN SILICIC ACID GEL

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Received September 30, 1933

Since the description of rhythmic formation of precipitates by Liesegang (10) in 1896, there have appeared several hundred articles (6) presenting numerous specific examples of this very common phenomenon, as well as many theories to account for the same.

If all salts precipitated uniformly in this manner, the diffusion wave theory of Wo. Ostwald (12) would probably suffice as an explanation. The failure of many compounds to behave in this manner and the numerous irregularities and varieties of periodic structure obtained have led to the propounding of numerous other theories. The theory of Bradford (1) involves the adsorption of the precipitate, that of Holmes (9) emphasizes the part played by the diffusion of the two reactants, and that of Dhar and Chatterji (3) introduces the idea of coagulation and peptization of the precipitate, which was further amplified by Hedges and Henley (7); all these theories are of considerable importance.

The studies on periodic precipitation in silicic acid gels which we have made emphasize the importance of a careful quantitative study of the phenomenon and indicate that a still more comprehensive study is desirable. A number of anomalous formations have been found which are not easily explained by any of the present theories, but not enough data have been assembled to allow an explanation to be attempted. In the present investigation, we have confined ourselves largely to a study of the effect of concentration on the phenomenon, that is, indirectly to a study of the effect of diffusion rate. Only incidentally will reference be made to any of the other factors which have been shown to influence banding. The work is being continued in the hope that sufficient data can be accumulated so that a satisfactory picture of the rôle played by diffusion rates may be formulated.

I. COPPER CHROMATE IN SILICIC ACID GEL

Stansfield (13) has reported the results of his work on the formation of bands of silver chromate in gelatin. His findings showed clearly that the greater the ratio between the concentrations of the salt in the solution and that in the gel, the farther apart were the bands. Although his study was carefully done, it was felt that with his data available a still more detailed investigation in another system would be of value. The precipitation of copper chromate in silicic acid gel was selected, as it is a very suitable reaction to study.

The silicic acid gel was prepared by mixing sodium silicate and acetic acid solutions. The sodium silicate solution was prepared by dilution of commercial sodium silicate, after settling and filtering, to a specific gravity of 1.060 ± 0.002. Upon titration against standard sulfuric acid, it was found to be 0.60 *N* ± 0.05. Acetic acid of 1.0 *M* strength was used, prepared *in situ* as described below.

Test tubes were cleaned with hot chromic acid, then alcoholic sodium hydroxide, rinsed with distilled water, and dried. Into each was introduced with a graduated pipet 0.50 ml. of glacial acetic acid. To each was then added the required volume of standard potassium chromate solution (0.50 *M*). The volume was then made up with water to 12.5 ml., giving a solution containing the desired concentration of salt and having an acid strength of 0.6 *M* (in the precipitation of all other salts, 0.75 ml. of acid was used, making a solution of 1.0 *M* strength). To each tube was then added 12.5 ml. of sodium silicate solution from a graduated pipet. The tubes were then stoppered and inverted. The air bubble was allowed to traverse the tube twenty times. The gels were very slightly basic, and set in about three minutes. After firm gels had been obtained (some hours), 5 ml. of a standard solution of copper sulfate was placed on top of each. The tubes were then tightly stoppered and the reaction proceeded.

TABLE 1

Concentrations of the salt in the gels and of the solutions on top of the gels

CONCENTRATION OF SALT IN GEL	CONCENTRATION RATIOS WHEN THE CONCENTRATION OF THE SOLUTION ON TOP OF THE GEL IS				
	0.5 *M*	0.4 *M*	0.3 *M*	0.2 *M*	0.1 *M*
M					
0.01	1:50	1:40	1:30	1:20	1:10
0.03	1:16.7	1:13.3	1:10	1:6.7	1:3.3
0.05	1:10	1:8	1:6	1:4	1:2
0.08	1:6.3	1:5	1:3.8	1:2.5	1:1.2
0.10	1:5	1:4	1:3	1:2	1:1

In this and most of the following studies, a series of twenty-five tubes was used. The concentration in the gel varied from 0.01 *M* to 0.10 *M* potassium chromate, while the concentrations on top were from 0.1 *M* to 0.5 *M* copper sulfate. Hence, the values of the concentration ratio lay between 1 and 50. This is more clearly indicated in table 1.

Observations were made daily on these earlier sets of tubes, until the reaction appeared to be complete. The liquid was then removed from the top and the cork tightly sealed in with shellac. The tubes were preserved practically unchanged for over three years.

A confirmatory series was later prepared by a modified technique which consisted of dissolving the weighed quantities of the salt in the standard acetic acid solution (0.5 *M* in this case). A series of these solutions was made up and 10-ml. portions placed in clean dry test tubes by means of a buret. To each was added 10 ml. of the standard sodium silicate solution and the contents thoroughly mixed as before described. These systems were allowed to stand, and when the gels became firm at the end of about twelve hours, 5 ml. of the other solution was placed on top of each gel by means of a pipet. The tubes were stoppered and allowed to stand.

In figure 1 is shown a series prepared by this modified technique and photographed after about one year. In this the effect of changing the concentration ratio can be seen. The number of bands decreased with the decrease of this ratio, as did also the space between corresponding bands, while the width of the bands increased. Marked irregularities are to be noted. These take the form of spirals in most cases, but well-formed washer-like bands were formed with the small center precipitated at a point slightly farther down the tube.

Stated in another way, as the concentration of the salt in the gel was increased and that on top held constant, the number and spacing of the bands decreased. Keeping the concentration in the gel constant, the effect of an increase in the concentration on top was to cause an increase in the number and spacing of the bands. These effects were noted throughout the entire series studied. Hence it becomes evident that in this case the concentration ratio may be varied by changing the concentration of either salt with exactly the same effect.

II. MERCURIC IODIDE IN SILICIC ACID GEL

This salt was prepared by diffusion of potassium iodide into gels containing mercuric chloride. A series of twenty-five tubes was prepared by the original technique. The concentrations used in the gel were from 0.001 *M* to 0.01 *M*, and those on top from 0.01 *M* to 0.05 *M*. The values used were one-tenth of the usual values, to prevent the formation of a large amount of precipitate, which tends to grow into long needles and obscure the banding.

In figure 2 are shown some of these tubes after reacting two months. The photograph was made three years later. The spacing is not as regular as with other systems. One very distinct effect does stand out, however, and that is that the space between the bands decreases toward the bottom of the tube. This effect has been observed in few other cases. Formation of the soluble double salt $KI \cdot HgI_2$ in the presence of excess potassium iodide accounts for the absence of precipitate in the upper portion of the tube. Reference to figure 2 shows also that the best bands are obtained when the concentration ratio is highest, and that the distance over which banding occurs is also greatest. This effect is produced by varying the concentration on top. Exactly the same effect is obtained by varying the concentration of mercuric chloride in the gel. This is shown in figure 3.

Dhar and Chatterji describe this salt as one belonging to their second class, and therefore there should be a decrease in the number and spacing of bands with increasing concentration. We find this to be true with increasing concentration in the gel, but not in the solution on top. It is still a question as to whether the effect of potassium iodide in redissolving the precipitate is sufficient to account for this. In the hope of obtaining more information about this system, a new series was prepared by the newer technique described above. Much the same results were obtained. The investigation is being continued.

III. COLLOIDAL MERCURY IN SILICIC ACID

Banding of colloidal mercury was first reported by Davis (2), who reduced mercurous nitrate with sodium formate in agar gel at a temperature of 53°C. Bands were evident, though not good. Orlowski (11) studied the reaction of ammonium hydroxide on mercurous nitrate in gelatin gels. He reports colored layers, followed by remarkable spiral bands. No references have been found to any study of this element in silicic acid gels, nor have either of these reported studies in other gels given any results comparable to the bands formed with common inorganic salts. The results of Davis, if interpreted in the light of some of the theories of banding, point

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FIG. 1. COPPER CHROMATE PRECIPITATES

In these tubes the concentration of the copper sulfate solution was 0.5 *M*, while the concentration of the potassium chromate in the gel was, reading from left to right, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10 *M*.

FIG. 2. POTASSIUM IODIDE-MERCURIC CHLORIDE-SILICIC ACID GEL SYSTEM

The concentration of mercuric chloride in the gel was constant at 0.003 *M*. The concentration of the potassium iodide solution on top of the gel decreased, from left to right, from 0.05 to 0.02 *M*.

FIG. 3. POTASSIUM IODIDE-MERCURIC CHLORIDE-SILICIC ACID GEL SYSTEM

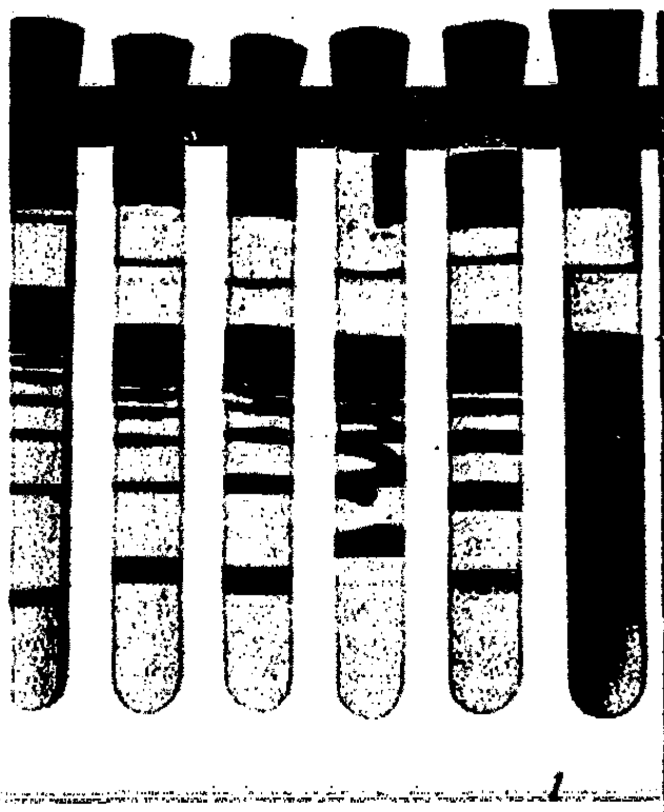
The concentration of the potassium iodide solution on top of the gel was constant at 0.04 *M*. The concentration of mercuric chloride, from left to right, was 0.01, 0.005, 0.003, 0.002, and 0.001 *M*.

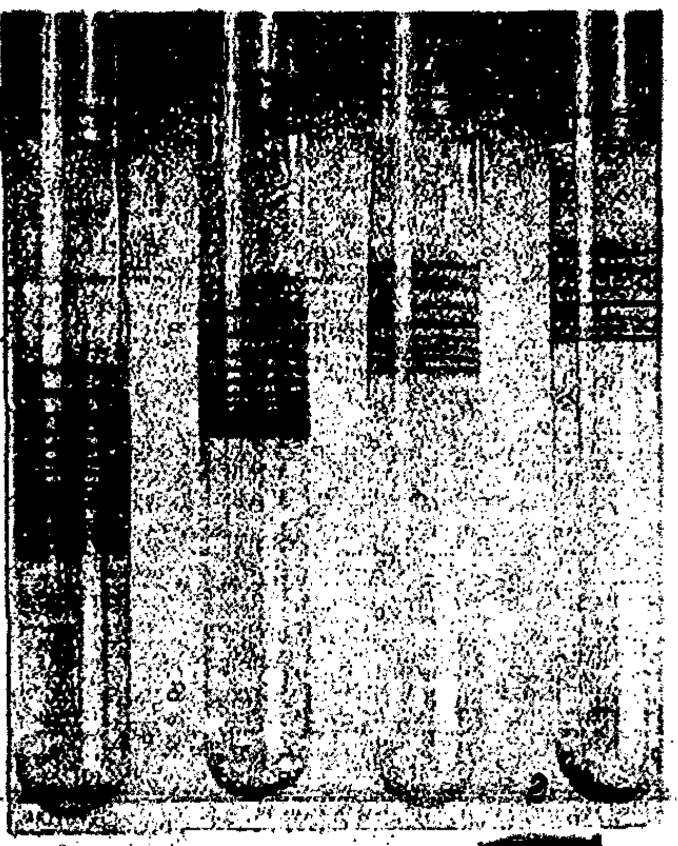
FIG. 4. MERCURY-SILICIC ACID GEL SYSTEM

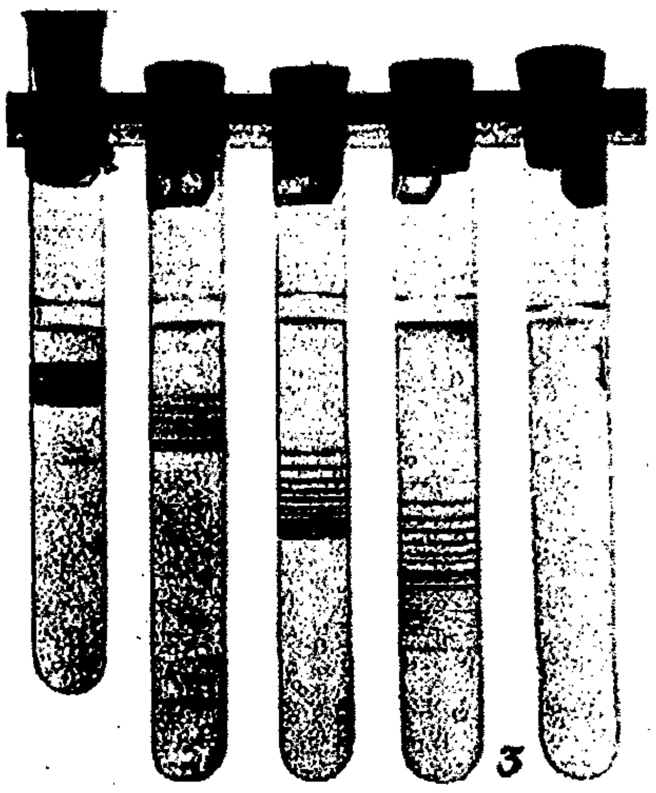
The concentration of the mercuric chloride in the gel was 0.1 *N*. Several portions of 0.2 *N* stannous chloride were used on top.

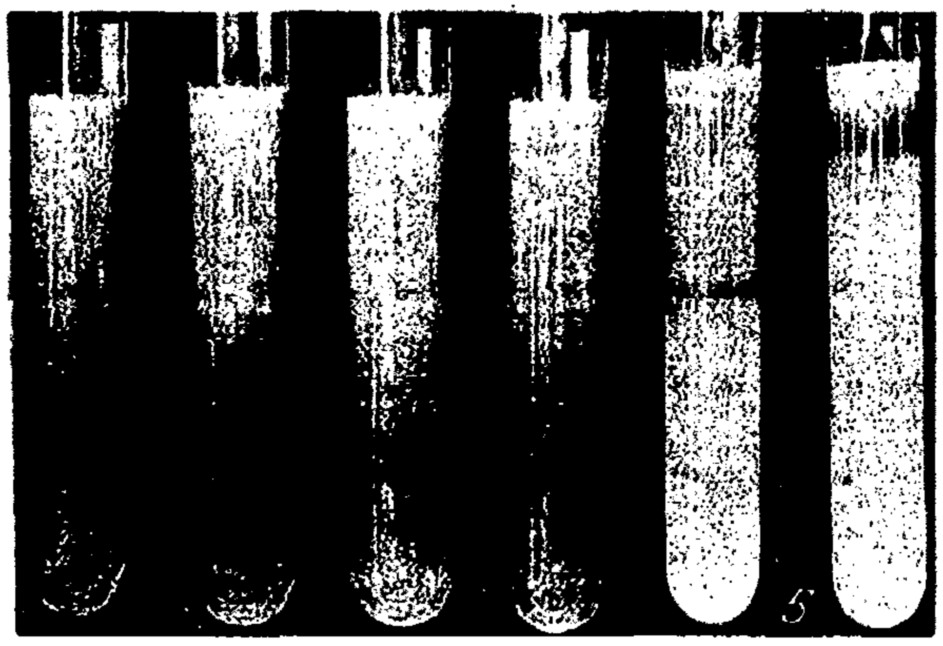
FIG. 5. LEAD ACETATE-POTASSIUM CHROMATE-SILICIC ACID GEL SYSTEM

The concentration of lead acetate on top of the gel was, from left to right, 0.4, 0.5, 0.4, 0.5, 0.02, and 0.02 *M*. The concentration of potassium chromate in the gel was, from left to right, 0.03, 0.04, 0.04, 0.03, 0.10, and 0.05 *M*.









FIGS. 1-5

toward the possibility of the supersaturation of a colloidal solution for which other evidence is lacking. Further, if the mercury be colloidal, the dispersoid is a liquid; diffusion of this liquid would result in annihilation of any bands which were formed.

We selected the reaction between mercuric chloride and stannous chloride as the most satisfactory procedure. Gels were made as described, except that 3 *N* sulfuric acid was used in place of *N* acetic acid, thus furnishing a strongly acid medium. Thirteen days were required for setting the gel. Saturated mercuric chloride was added to four times its volume of the silicate-acid mixture and 0.2 *N* stannous chloride was employed on top. During thirty-eight days of reaction the stannous chloride was renewed several times.

White bands of what was evidently mercurous chloride progressed down the tube. These later became bands of black mercury and mercurous chloride alternately. Finally, bands of black mercury were all that could be observed. The spaces were very narrow in some parts of the tubes, but very distinct.

These bands are shown in figure 4. The photograph was taken three years later, and the tubes are somewhat damaged by drying. The dense region near the top contains fine bands which do not show in the figure.

Reduction of mercurous nitrate with sodium formate at room temperature proved unsuccessful. Stannous chloride reduced mercurous nitrate to mercury, but without the formation of bands.

IV. LEAD COMPOUNDS IN SILICIC ACID GEL

1. *Bands of lead chromate*

It is well known that lead chromate and silver dichromate had not until recently been made to band in silicic acid gel. Dhar and Chatterji (4), upon the basis of their theories, attempted to show why these two did not form bands in silicic acid gel. A zone of peptizing values was found inside of which banding did not occur readily. The values for these two salts were believed to lie outside this zone, i.e., the peptizing influence of the gel was too strong to allow banding to occur.

Later, Hatschek (5) showed that silver dichromate could be made to band in silicic acid gel. We have now been able to produce bands of lead chromate in silicic acid gel.

Several series of tubes were prepared by the first technique. After several months reaction they were sealed and preserved. The bands in these tubes were perfectly clear and definite. They were very narrow, and made up of long needles which tended to obscure the bands. For these reasons it was impossible to secure satisfactory definition in photographs of them.

Again, when the concentration in the gel was constant, the distance over which banding occurred varied directly as the ratio of concentrations. Since in practically all tubes the amount of solution on top was in excess, the constant concentration in the gel should have predetermined a fixed and constant amount of precipitate. The spacing between the bands was wider as the ratio was increased, as found in the other cases reported.

When the concentration on top was held constant (and in excess), the decrease in ratio caused a decrease in the spacing of the bands and in the region in which they were formed. In this case the total quantity of precipitate varies with the concentration in the gel, and is greatest in those tubes in which the distance in which bands were formed is least. Another feature noted throughout the whole series was that bands were closer together near the bottom of the tubes.

It was found difficult to repeat the banding by this technique. The uncertainty of obtaining bands, and their close packing and indistinctness, lend some support to the theory of Dhar and Chatterji that the peptization value for this salt in silicic acid lies near the boundary line. But our observations show that the actual value is probably just within rather than just without the precipitation value.

Later several series of tubes were prepared by the newer technique. The banding was more pronounced and was easy to duplicate. A number of these tubes are shown in figure 5.

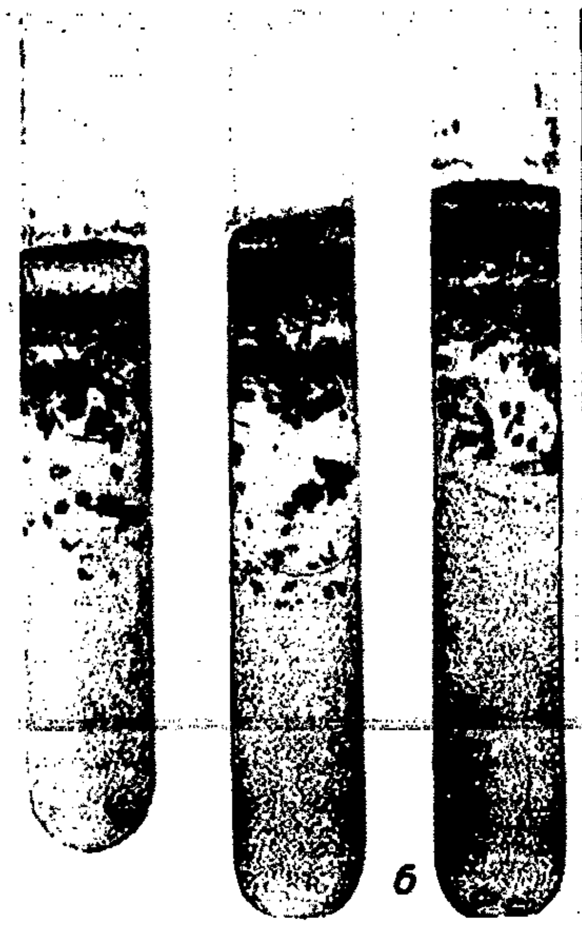
2. *Lead iodide*

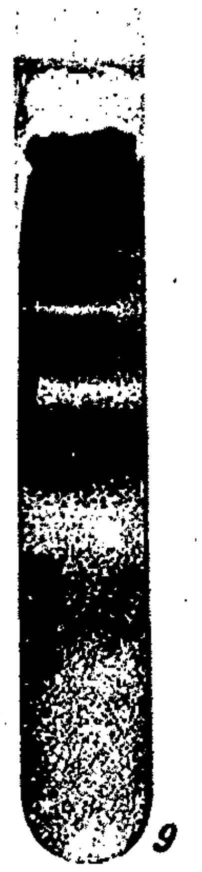
A series of tubes was made as above, with potassium iodide in the gel and lead acetate on top. The concentration ratios were the same as for lead chromate.

The lead iodide formed large hexagons as usual, but these were arranged in quite definite bands. Measurement of distances was impossible but the banded appearance is unmistakable, as shown in figure 6.

In those tubes in which the concentration of potassium iodide in the gel was less than 0.03 *M* there was no precipitation of lead iodide, although some white crystals appeared in the liquid or imbedded in the surface of the gel. When the concentration reached 0.05 *M*, some crystals appeared in the lower portion of the tube, and it was not until a concentration of 0.10 *M* had been reached that good crystals were formed. The same effects of changing concentration ratio were noted as in the other cases.

By means of the new technique, more series were prepared, and again precipitates occurred in the most concentrated members. Finally, a third series was prepared in which the position of the reactants was reversed. These gave very much better results, forming very large beautiful crystals, but no evidence of bands. This is shown in figure 7. However in all cases the abundance and depth to which the crystals formed was proportional to the increase in the concentration of potassium iodide.





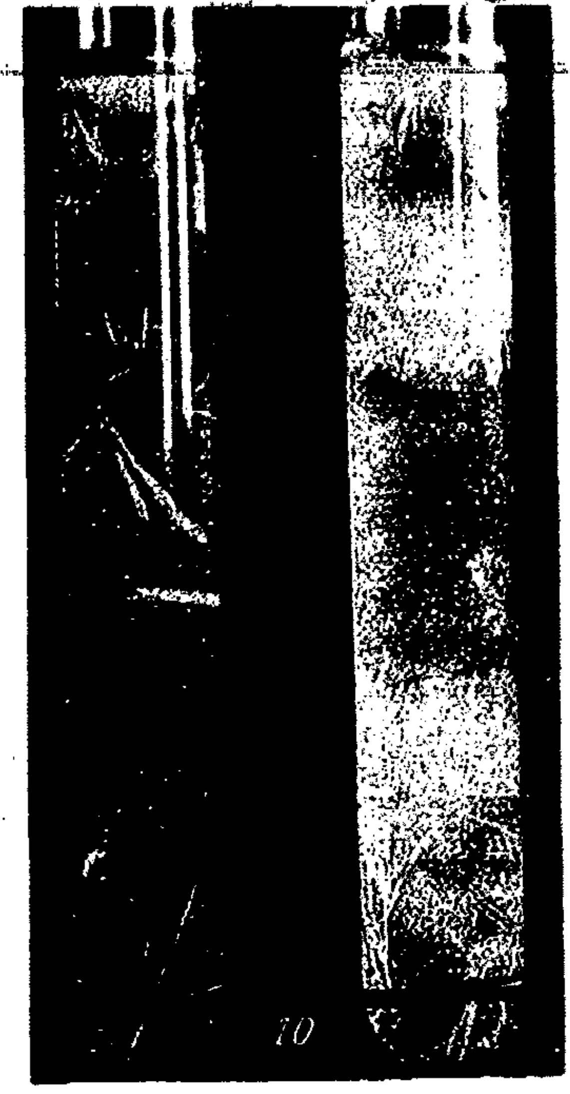


Fig. 6. Showing the Banded Structure of Lead Iodide

Fig. 7. Lead Iodide in Silicic Acid Gel

The concentration of potassium iodide on top of the gel decreased, from left to right, from 0.5 to 0.05 *M*. The concentration of lead acetate was 0.02 *M* in all tubes.

Fig. 8. Lead Bromide in Silicic Acid Gel

The concentration of lead acetate on top of the gel, increasing from left to right, was 0.2, 0.3, 0.4, and 0.5 *M*. The concentration of potassium bromide in the gel was constant at 0.05 *M*.

Fig. 9. Lead Sulfate in Silicic Acid Gel

Fig. 10. Lead Formate in Silicic Acid Gel

Again, since this was in excess in almost all tubes the amount of precipitate should depend upon the amount of lead acetate present, which was constant.

We conclude from this, that although these crystals grow large and obscure any evidence of bands, one of the factors is still operating, namely that which governs the quantity and distribution of the precipitate. Apparently, either this factor is independent of that which produces the banded structure, or in this case some other factor operates to prevent the formation of small crystals in bands.

3. *Lead bromide*

Lead bromide has been found to band in gelatin, but in silicic acid gel Holmes (8) reports that under the conditions of his experiments only white twin crystals were formed. We have prepared a concentration series, and among the tubes were found a number exhibiting marked banding. This is shown in figure 8. The bands were, however, almost "opacity" bands, the density of precipitate being very low. It was thought that the potassium acetate formed in the reaction acted to dissolve the lead bromide.

By means of the newer technique, other series were prepared which exhibited only the white twin crystals. Just as in the case of lead iodide, the depth to which the precipitate forms varies directly with the concentration of the solution on top, whereas the quantity should be determined by the much smaller amount of the salt contained in the gel.

4. *Lead sulfate*

There seems to be no definite information about the precipitation of this salt in silicic acid. We found that a tube containing 0.1 *M* lead acetate in contact with 0.2 *M* ammonium sulfate solution showed excellent bands after two months. One of these tubes photographed three years after it was prepared is shown in figure 9.

Following this a number of concentration series were prepared by the usual method, using potassium sulfate in the gel reacting against lead acetate. There was a marked tendency to band, but the crystals were large and scattered, and the banding was a rhythmic concentration of crystals. The quantity and distribution of the precipitate varied exactly as did that of lead iodide and bromide. Recent experiments show that the use of ammonium sulfate produces much better banding than potassium sulfate.

5. *Lead formate*

Concentrated formic acid was allowed to diffuse into a gel 0.1 *M* with respect to lead acetate. Nothing at all appeared for several days. Then suddenly, areas of precipitation appeared throughout the tubes, particularly near the bottom. These grew out into long branching masses in a few hours. During the course of a week these crystals continued to grow, becoming thick and club-like. The reaction was repeated a number of times with similar results. Two of these tubes are shown in figure 10.

This sudden appearance of the precipitate in all parts of the tube at once makes the system of particular interest. Diffusion throughout the whole tube must have taken place with the formation of a supersaturated solution, which suddenly precipitates. Since no evidence of bands can be noted, it appears that this is strong evidence against the precipitation of a supersaturated solution yielding a rhythmic structure, as Ostwald contends.

V. BISMUTH COMPOUNDS IN SILICIC ACID GEL

The citrate, oxalate, iodide, and basic dichromate were prepared in silicic acid gel. No evidence of bands was observed in the case of the first two. Strong citric acid diffusing into a gel $N/25$ with respect to bismuth nitrate gave after several days bunches of crystals resembling cotton and distributed throughout the tube. Supersaturation was again indicated. Saturated oxalic acid diffusing into a gel prepared in the same way gave only tree-like formations of flat, silky crystals.

The basic bismuth dichromate was prepared in a gel formed from two parts of the silicate solution to one of N acetic acid. A small crystal of potassium dichromate was added. The gel set in two minutes and $N/5$ bismuth nitrate was placed on top immediately.

A bright yellow coloration progressed down the tube. Following this, bands of a yellow precipitate formed. They were perfectly plane, well-formed, and very thin. There were many holes in them. In all tubes, five rings formed in a space of about 3 cm.

Potassium iodide diffusing into a gel containing bismuth nitrate produced a heavy reddish brown precipitate. Reversing the reagents gave a yellow ring of color which progressed down the tube. It was followed by a heavy brown precipitate, and finally by well-formed black crystals which appeared to be iodine. A concentration series was attempted, and in every case these black crystals formed, and in many cases grew to be long feathery trees. A great deal of gas was liberated also.

VI. SUMMARY AND CONCLUSIONS

A study of the most favorable ranges of concentration for the formation of banded precipitates of copper chromate, mercuric iodide, mercury, lead chromate, lead iodide, lead sulfate, and basic bismuth dichromate in silicic acid gel has been made. No bands were, however, obtained of lead bromide, lead formate, bismuth oxalate, bismuth citrate, and bismuth iodide.

The pairs of salts were so arranged that in one series one of the pair of reacting salts was in the gel, and in another series the other salt was in the gel. In many cases the results were markedly different.

In all of the salts which were prepared in a concentration series, it was found that if the concentration in the gel was kept constant and that of the solution varied, the depth to which the precipitate formed and the number of bands formed was in proportion to the increase in concentration of the salt in the solution. It was also found that if the concentration in the solution on top was kept constant and that in the gel varied, the depth to which the precipitate formed and the number of bands decreased with the increase in concentration of the salt in the gel.

In general, the width of the bands and the spacing between them increased as the bottom of the tube was approached. We have found two marked exceptions to this, namely, mercuric iodide and lead chromate. Both of these gave numerous bands composed of fine crystals, in which the width of the spaces between the bands decreased toward the bottom of the tube.

It has been found that in those systems in which the concentration ratio was greatest, the banding was best and extended farthest into the tube. In those systems of lower concentration ratios there was rarely any banding.

In addition to this, it was found that in those systems in which banding did not occur, the depth to which precipitates were formed was likewise proportional to the magnitude of the concentration ratio. Therefore it appears that the rate of diffusion, which is approximately proportional to this ratio, is the controlling factor in the distribution of the precipitate.

In the case of lead chloride, lead bromide, and mercuric iodide the additional factor of re-solution of the precipitate by one of the soluble salts seems to be important. The idea that banding is a result of precipitation of a supersaturated solution does not seem to be confirmed by our results on lead formate. The quantitative studies of the concentration relations now in progress in this Laboratory will add some valuable data and we hope will help in the solution of some of these problems.

The interesting phenomenon of the banding of liquid metallic mercury has been recorded.

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PECTIN STUDIES. III

General Theory of Pectin Jelly Formation

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Received August 24, 1933

Most of the recent work on the chemistry of the pectin molecule fails to consider that pectins may vary depending upon their source. Even among those who have considered the pectins on the basis of their physicochemical properties, there appears to be a school of thought which favors the view that pectins of whatsoever source are the same and that such differences as are observed are to be considered as due merely to impurities present (6). It has, however, long been recognized commercially that citrus and apple pectins, irrespective of grade, form jellies of definitely different types, although this difference has not generally been recognized in scientific pectin literature.

APPLE AND CITRUS PECTINS

In two earlier papers (7, 11) of the present series the interrelationship of sugar, acid, and pectin was considered for citrus pectin and for apple pectin, respectively.

Whatever the grade of pectin used, the type of jelly obtained remains typical of either citrus or apple. The former jellies are comparatively friable, with little elasticity, while the latter jelly is highly elastic. It is a common observation that apple pectin jellies require—in fact, tolerate—much less acid than citrus pectin jellies similarly prepared. It has also been observed in this laboratory that pectins from other sources, such as cranberry and turnip, differ markedly in their characteristics from either of the above.

THE "OPTIMUM ACIDITY" CONCEPT

A number of explanations of "optimum acidity" as related to pectin jellies have been offered by various investigators since Goldthwaite (3) in 1909 first called attention to the importance of acid. Lal Singh (9) demonstrated that the necessary acid may be reduced by increasing the sugar concentration. However, Tarr (12) and Baker (1) for the first time placed the matter on a definite quantitative basis not only by measuring the acidity in terms of pH but by devising a means for expressing jelly strength accurately. These authors repeatedly suggested that the optimum acidity indicated a stoichiometric relationship between pectin and acid. Spencer (10) in 1929 insisted that Tarr and Baker's optimum was related to the hot method only. She presented data to show that with a cold method, that is, the mixing at room temperature of a sugar syrup, acid, and pectin solutions, there is observed a minimum acid requirement, but no maximum acid limit. She suggested that the turning point in the jelly strength curve, called "optimum acidity" by Tarr et al., "might simply mean that at this hydrogen-ion concentration the decomposition of pectin begins to predominate over the increased strength due to increased acidity." The present writer has elsewhere suggested that data obtained for citrus pectin do not conform to these interpretations (7), and Cole, Cox, and Joseph (2) have indicated that jelly failures past the optimum acidity may be caused by the increased rate of setting. It appears to the present author that a few simple concepts from colloid chemistry may suffice to explain quite satisfactorily the observed phenomenon.

Kruyt (4, 5) has outlined a concept of the stability factors operating in a system containing the emulsoid agar-agar. His views may readily be translated into terms of pectin, sugar, and acid. Granted that pectin is a negatively charged hydrophilic colloid we may assume the following:

(1) The sugar functions as the dehydrating agent.
(2) The hydrogen-ion concentration functions by reducing the negative charge on the pectin, thereby permitting the pectin to precipitate and coalesce in the form of a network of insoluble fibers, providing the concentration of the sugar is sufficiently great.
(3) The dehydration of the pectin particle by sugar is not instantaneous but requires time to come to an equilibrium.
(4) The rate of dehydration and precipitation increases directly as the hydrogen-ion concentration.
(5) The maximum jelly strength is reached when the system reaches equilibrium, and depends upon the position of that equilibrium.
(6) Any component added to a pectin jelly system, including salts, which causes a change in the ultimate jelly strength of that system may function either (a) by changing the rate of gelation, or (b) by affecting the position of the ultimate equilibrium of the system, or (c) by a combination of these two effects.

In any given jelly mixture the rate of precipitation and orientation of fibers or micellae will go on at a rate varying directly with both sugar concentration and hydrogen-ion concentration and each pectin–acid–sugar combination will have a time limit, inherent in the procedure, at which the jelly structure is so well formed that any mechanical disturbance will reduce the ultimate perfection and therefore the strength of that structure. It is to be assumed that temperature will be an additional factor in these relationships. On this basis for a given time–temperature–pectin–sugar combination, that is, for any given empirical jelly-making procedure, there must be a maximum hydrogen-ion concentration which results in a rate of gelation that barely permits the completion of the procedure within the time limit of the system. This would be the optimum acidity for that particular combination.

From this viewpoint the changes observed with varying sugar concentrations become logical. The disappearance of an optimum at the lower sugar concentrations simply means that the rate of pectin precipitation has become sufficiently slow at all acid concentrations so that the time factor does not enter. Likewise the absence of an optimum in Spencer's jellies does not distinguish a cold method from a hot method, but simply indicates that she operated within the time limit of the system. In other words, the "optimum pH" may be considered purely manipulative in character and is that hydrogen-ion concentration in any given procedure at which premature gelation becomes a measurable factor in the jelly strength of the finished jelly.

On the above basis we may postulate that: (1) Other types of pectin will show a behavior similar to that of citrus pectin, although not necessarily at the same proportions of sugar and acid. Using the same short-boil empirical method as previously used there should be for each pectin some sugar level at which the rate of jelly formation becomes sufficiently slow so that the so-called optimum disappears. (2) The optimum pH may be made to pass through these same stages by merely changing the time relationship of the process.

APPLE PECTIN

The above postulates were considered in our observations on apple pectins. The experimental procedure was identical with that previously described (7). In order to obtain a greater variation in acidity, phosphoric acid was used instead of tartaric acid. The acid was added in the form of a 25 per cent solution, allowance being made for the amount of water thus added. The pH of the finished jelly was determined by the quinhydrone method (11). The apple pectin used, 119F, is an alcohol-precipitate from Certo. Details of procedure and the results obtained appear in table 1 and figure 1. It may be noted that although the characteristics of this pectin are definitely different from those previously shown for citrus pectin, nevertheless a sugar concentration can be found in each case at which the rate of gelation is such that no definite optimum is shown. For 119F this is at 50 per cent sugar. The 60, 55, and 50 per cent curves for 119F resemble respectively the 70, 65, and 60 per cent curves previously shown for citrus pectin. This is in agreement with postulate 1.

TABLE I

Effect of sugar concentration on "optimum acidity" and jelly strength of apple pectin jellies (119F alcohol-precipitated pectin)

All series of jellies identical except for sugar concentration. 2.5 g. of pectin 119F and the indicated amount of acid was used. Final net weight of jelly 555 g. Total heating time, about 4¾ minutes. See also figure 1.

25 PER CENT PHOSPHORIC ACID PER BATCH OF JELLY	SUGAR CONCENTRATIONS							
	50 per cent		55 per cent		60 per cent		70 per cent	
	J.S.*	pH	J.S.	pH	J.S.	pH	J.S	pH
cc.								
0.15	—	—	—	—	0	3.34	50	3.62
0.25	—	—	—	—	—	—	65 66	3.40 3.35
0.30	—	—	—	—	11.5	3.21	60	3.27
0.35	—	—	—	—	—	—	62	3.24
0.40	—	—	—	—	40	3.06	55†	3.09
0.50	—	—	11	2.87	63	2.92	[32]	2.93
0.55	—	—	—	—	61	2.81	—	—
0.60	5	2.67	—	—	57	2.74	—	—
0.70	—	—	43	2.61	—	—	—	—
0.80	—	—	47 51	2.53 2.50	39	2.46	—	—
0.90	18.5	2.41	51	2.42	—	—	—	—
1.00	—	—	42	2.39	39.5	2.34	—	—
1.20	21.5	2.22	—	—	—	—	—	—
1.40	—	—	34‡	2.26	29	2.16	—	—
1.50	31	2.12	—	—	—	—	—	—
1.60	—	—	27	2.10	21	2.02	—	—
1.80	—	—	25.5	1.98	—	—	—	—
2.00	26	1.98	21.5	1.94	[12]	1.92	—	—
2.50	26	1.83	—	—	—	—	—	—
3.00	31	1.79	24.7	1.73	—	—	—	—
3.50	27	1.72	—	—	—	—	—	—
4.00	27.5	1.66	—	—	[11]	1.62	—	—
5.00	27	1.59	32	1.61	—	—	—	—
10.00	33	1.37	36.5	1.37	[9]	1.20	—	—
35.00	31	1.05	31§	0.86	[9]¶	0.98	—	—

* Jelly strength.

† 0.42 cc. of acid.

‡ 1.3 cc. of acid.

§ 40 cc. of acid.

¶ 30 cc. of acid.

Figures in brackets indicate "curdled" jellies.

It becomes apparent from a study of these curves that for most practical purposes jellies containing 60 to 65 per cent sugar should be preferable. In all cases the further lowering of sugar concentration carries the penalty of lower jelly strength and greater acid requirement. This lowering of jelly strength may be assumed to be due to incomplete dehydration and therefore either incomplete precipitation or a more flexible network of pectin.

THE TIME FACTOR CONCEPT

The second postulate made above was first tested by preparing jellies in the manner suggested by Spencer, except that the temperature of the jelly mixture was 55°C. instead of room temperature. This allows a greater time factor without involving any measurable hydrolysis of the pectin. The jellies made were 60 per cent. The pectin used was the 119F used in previous observations and the amount used identical with the prior series.

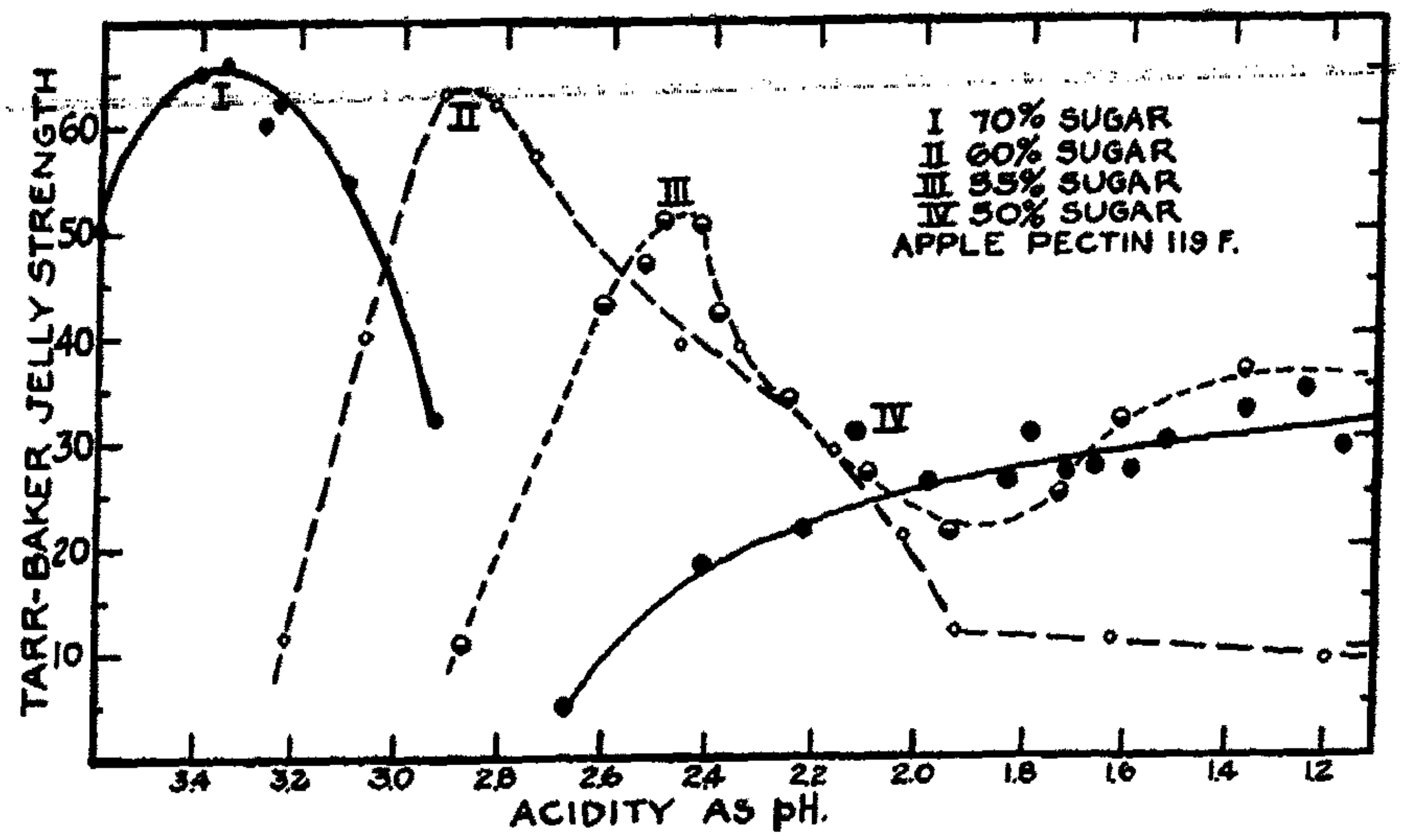

FIG. 1. EFFECT OF SUGAR CONCENTRATION ON OPTIMUM pH AND JELLY STRENGTH OF APPLE PECTIN JELLIES

Phosphoric acid used

The 2.5 g. of pectin and 30 g. of sugar were dissolved in just enough water to make a total of 140 g. and brought to 36°C. The sugar, the minimum amount of acid used, and the remaining water were boiled together, cooled to 65°C., and adjusted to correct weight with distilled water. The additional acid was then added and the pectin solution rapidly stirred in while the beaker remained immersed in a water bath at 55°C. The temperature of the jelly mixture was in each case 55°C. Allowance was made in all weights for the amount of pectin solution remaining in the original beaker.

Three series of jellies were made, varying the acid within the same limits used in previous series. For series A the total mixing time from the moment the pectin solution was poured into the warm syrup until the mixture was poured into the glasses was exactly 8 seconds; for series B the time was 50 seconds; for series C the time was 90 seconds. The results in every way conformed to the postulate made. The magnitude of the jelly strength for the 8-second series was quite remarkable, indicating that under the conditions of the usual hot method even at the optimum point only a fraction of the true jelly strength is obtained. The results are listed in table 4 and are shown graphically in figure 2 along with the corresponding 60 per cent curve from table 2. There is also shown a curve obtained in a manner identical with the latter except that an additional 80 cc. of distilled water was added to each batch of jelly, thereby changing the heating time from $4\frac{3}{4}$ to 10 minutes. The final net weight was the same in all cases.

TABLE 2

The relation of the time factor to optimum acidity

The time indicated is the interval between the pouring of the pectin solution into the sugar syrup and the pouring of the mixture into the glasses. Jellies contain 60 per cent sugar, 2.5 g. apple pectin 119F, phosphoric acid as indicated. Temperature of pectin solution, 36°C.; of sugar solution, 65°C.; of final mixture, 55°C.

25 PER CENT PHOSPHORIC ACID	SERIES B 90 SECONDS		SERIES C 50 SECONDS		SERIES D 8 SECONDS	
	J.S.	pH	J.S.	pH	J.S.	pH
cc.						
0.26	—	—	0	3.27	—	—
0.36	33	3.10	—	—	36.5	3.13
0.56	69	2.80	—	—	67	2.88
0.86	—	—	80	2.50	—	—
0.96	41	2.39	—	—	115	2.40
1.06	—	—	75	2.37	—	—
1.26	—	—	61.5	2.24	—	—
1.56	19	2.13	—	—	120	2.13
1.96	14.5	2.03	28.5	2.00	145 (?)	2.01
3.96	—	—	—	—	135	1.76

One may consider the data shown in figure 2 as those of five investigators using methods A_1, A_2, B, C, and D in their individual studies of the same pectin 119F. It is apparent that A_1 and A_2 would conclude that this particular pectin had an optimum pH of either 2.96 or 2.90. B would place the optimum for the same pectin near pH 2.8, and C about pH 2.6, while D would conclude that the maximum jelly strength is not reached without sufficient acid to give a pH of 2.0 or less, and that apparently we cannot have too much acid.

It still remains true, however, that *with any given procedure* the acid relationship of each type of pectin is a definite characteristic which must be carefully considered in order to obtain best results. Evidently the factor which is most involved is the rate of gelation of the pectin as affected by the acid. The largest or "optimum" amount of acid to be used will be that point at which an additional increase of acid will increase the rate of setting to a point where loss in jelly strength due to a disturbance of the jelly in the stirring or pouring exactly balances the strengthening effect of that same increment of acid. Such observations emphasize the necessity for close adherence to a given empirical method of jelly making in any systematic study of the factors involved.

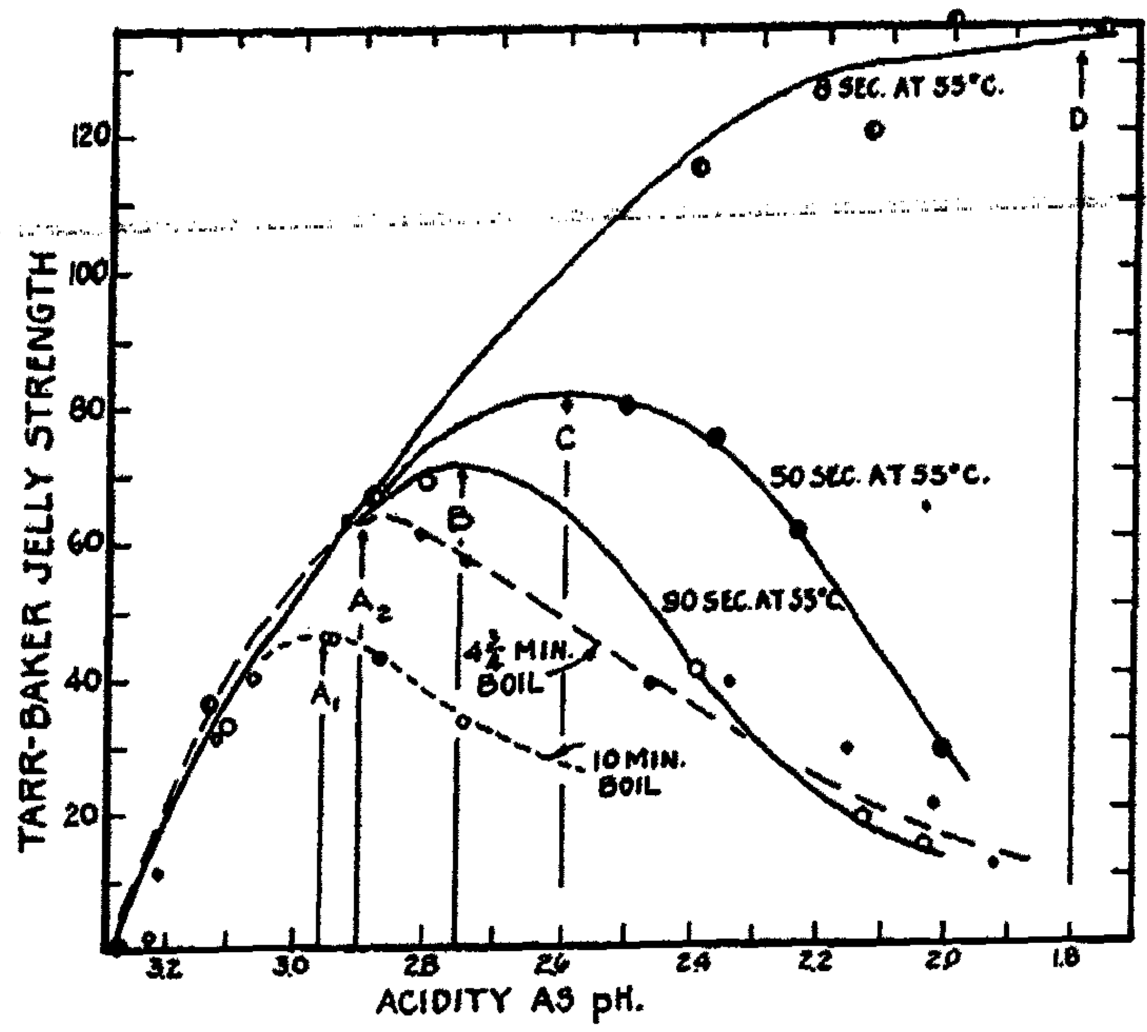

FIG. 2. EFFECT OF METHOD OF MAKING JELLY UPON "OPTIMUM ACIDITY"

60 per cent sugar; apple pectin 119F; phosphoric acid

THE TEMPERATURE FACTOR

The abnormally high jelly strengths obtained at 55°C. cannot be explained on the basis of the time concept. Apparently the usual high temperature of jelly making either destroys a large proportion of the pectin value, or the character of the gel structure obtained at the lower temperature differs from that formed from a hot mixture.

For a number of years it has been a common commercial procedure to place the acid solution in the container into which the non-acidified pectin–sugar–water mixture is subsequently poured. This practice was shown by Stuewer, Beach, and Olsen (11) to eliminate the so-called optimum peak when the jellies were poured at 96°C. The mixing by pouring is almost instantaneous, but the jelly strengths did not differ greatly from those observed at optimum using the regular method. On the basis of the time factor curves shown in figure 2, it did, however, seem reasonable to expect that this method, which permits of maintaining mixing time at a minimum, should show a rise in jelly strength as the temperature of pouring is lowered from 100°C. to room temperature. Accordingly several double batches of non-acidified pectin jelly mixtures were prepared by the usual hot method. After quickly cooling the mixtures to a desired temperature, with proper adjustment for loss in evaporation, the syrup was poured into a series of eight glasses containing varying amounts of 10 per cent phosphoric acid solution plus water to make 2 cc. Rapid pouring results in efficient mixing of acid, no stirring being necessary; in fact at the lower temperatures the "set" was so rapid that stirring was not desirable.

TABLE 3

Effect on jelly strength of preparing jelly mixture without acid, cooling to different temperatures, and pouring into glasses containing varying amounts of acid

60 per cent sugar; 2.5 g. of 119F pectin in 555 g. of jelly; acid as indicated

GLASS NO.	10 PER CENT PHOSPHORIC ACID	WATER	JELLY STRENGTH AND pH VALUES OF JELLIES POURED AT THE FOLLOWING TEMPERATURES														REGULAR PROCEDURE	
			100°C.		90°C.		80°C.		70°C.		60°C.		50°C.		40°C.			
			J.S.	pH	J.S.	pH	J.S.	pH	J.S.	pH	J.S.	pH	J.S.	pH	J.S.	pH	J.S.	pH
	cc.	cc.																
1	0	2.0	0	3.66	—	—	—	—	—	—	—	—	—	—	—	—		
2	0.20	1.80	13	3.11	19	3.09	14	3.12	14	3.13	13.5	3.21	—	—	—	—		
3	0.30	1.70	38	2.94	37	2.85	40	2.84	45	2.89	35	3.00	—	—	—	—	34.5	2.83
4	0.40	1.60	39	2.74	36	2.70	32?	2.68	42	2.62	47	2.68	64	2.73	69	2.85	37+	2.68
5	0.60	1.40	42	2.38	45.5	2.35	43	2.48	40	2.40	45	2.42	86	2.33	85	2.58	31.5	2.52
6	0.80	1.20	38	2.23	47	2.23	45	2.23	46	2.25	59	2.19	80	2.31	92	2.35	25	2.31
7	1.0	1.0	38	2.14	57	2.11	48.5	2.11	55	2.15	64.5	2.15	76	2.19	100	2.18		
8	2.0	0	35	1.85	48	1.86	49	1.89	62	1.85	65	1.89	97	1.88	93	1.88		
8a	2.0	0	40	—	49	—	52	—	—	—	—	—	86*	—	—	—		
8b	2.0	0	40	—	—	—	—	—	—	—	—	—	—	—	—	—		

* 55°C.

The results are given in table 3 and figure 3. The figures obtained are rather irregular. It should be noted, however, that each point plotted on the graph represents only one measurement on one glass of jelly, while usually such points represent the average of four jellies. Considerable variation was therefore to be expected. Nevertheless, the trend of these results is quite apparent, and it can be stated that repeated tests with other samples of apple pectin invariably showed similar differences in jelly strength between jellies poured at varying temperatures.

It remained to determine whether the low jelly strengths obtained at 100°C., as compared with the high values obtained at 50°C., were due to acid destruction of the pectin at the higher temperature or to a tendency of the pectin to set differently from a hot solution than from a cool solution. In this connection it should be borne in mind that the very rapid setting at 50°C., compared with the somewhat slow set of jellies poured at 100°C., is unfavorable to uniform mixing of the acid and jelly mixture at the lower temperature. One might, therefore, logically expect a less perfect jelly at the lower temperature.

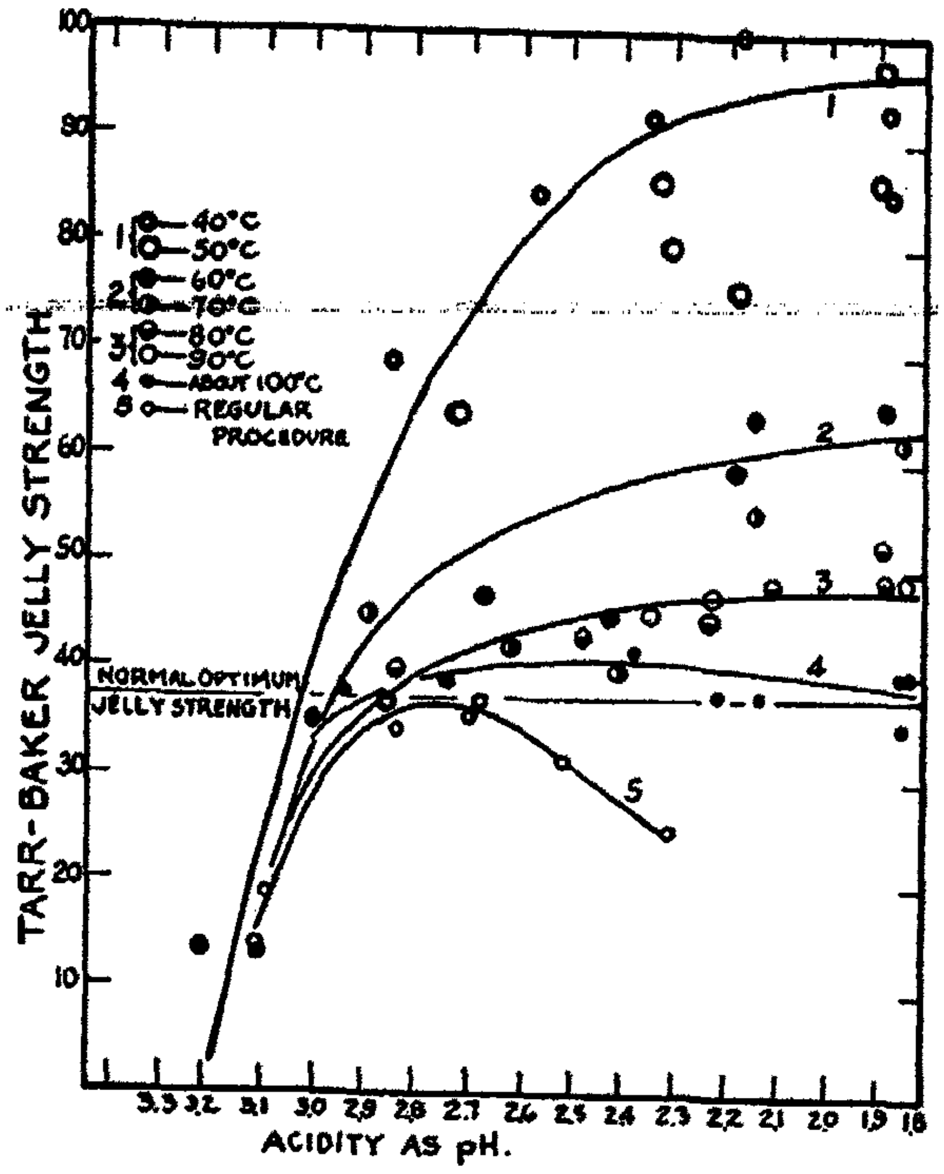

FIG. 3. EFFECT OF TEMPERATURE AND METHOD OF PREPARING JELLIES UPON SO-CALLED OPTIMUM pH AND MAXIMUM JELLY STRENGTH OF APPLE PECTIN 33F

This question was answered by recovering the pectin from duplicate batches poured (a) at 100°C. and (b) at 50°C. and remaking the recovered pectin into jellies, both of which were poured at 50°C. This procedure was repeated. In each case the pectin from the low-strength jelly when remade into the same amount of jelly at 50°C. gave a jelly strength practically equivalent to that obtained with pectin recovered from the high-strength jelly. This is conclusive proof that the lower strength of the jellies prepared by pouring at 100°C. is not due to hydrolysis of the pectin by the acid. Evidently the rapid set at the lower temperatures results in a different and stronger gel structure. This is contrary to experience with gelatin, where it was found that slow setting at a higher temperature resulted in better jelly formation than quick setting at low temperatures (8).

It was thought of interest to determine whether in the course of time jellies identically prepared, except for the temperature of pouring, would tend to approach the same equilibrium in jelly strength. Results indicate the contrary. Observations over a period of four weeks show the high-strength low-temperature jellies to increase in strength at a more rapid rate than the low-strength jellies poured at 100°C. These results are tabulated in table 4. The details of the experiments were as follows:

TABLE 4

The effect of temperature of contact with acid upon jelly strength and upon pectin grade

NO.	TEMPERATURE OF POURING	JELLY STRENGTH*	JELLY STRENGTH WITH RECLAIMED PECTIN (POURED AT 50°C.)*
	°C.		
1	100	53	90
2	50	118	98
3	100	55	112
4	50	132	135

NO.	TEMPERATURE OF POURING	JELLY STRENGTH†				
		1st day	3rd day	8th day	2 weeks	4 weeks
	°C.					
5	100	35	39	43	42	43
6	50	87	116	115	131	122

* Each figure the average of four determinations.

† Each figure the average of two determinations.

Five grams of pectin, 800 g. of sugar, and 545 cc. of water were brought to a boil in the usual manner and cooked to a net weight of 1313 g. From this batch four glasses, each containing 2 cc. of 10 per cent phosphoric acid, were filled at 100°C. (total, 555 g. of jelly). The remaining syrup was cooled rapidly to 50°C., adjusted for loss by evaporation, and four glasses, each containing 2 cc. of 10 per cent phosphoric acid, were filled at that temperature. The extra syrup was discarded. After standing overnight the jelly strength was determined and identical amounts of each batch (as nearly 555 g. as possible) were cut into small pieces and steeped in 60 per cent alcohol. The alcohol was changed three times in the course of that many days. Finally the pectin jelly was drained on a cloth, washed with strong alcohol, squeezed dry, and at once dissolved in sufficient water for the preparation of a standard batch (555 g.) of jelly. These jellies were both poured at 50°C. The entire procedure was subsequently repeated.

The results throw an interesting light upon the pectin gel formation. Apparently the structure of the jelly is fundamentally different when slowly set from the hot solution than when rapidly set from the cool syrup. If we assume that pectin exists in two states of hydration, that is, if the amount of water bound by the pectin fibrils differs depending upon the temperature at which the pectin is precipitated, then a ready explanation is at hand.

Summing up the entire thesis one may say that in the ideal pectin jelly system each increment of acid functions in two ways, although these fundamentally may be counterparts of the same function: first, the rate of gelation is increased towards a maximum; second, the strength of the ultimate gel structure is increased towards a maximum. When in any system the time factor does not interfere with the maximum rate there will be no optimum acidity (curve D). If, however, at some point the rate of gelation crosses the time boundary of the system, that point will be the optimum for that system because further increases in rate of gelation will be increasingly interfered with until the maximum rate of gelation is reached, at which point further increments of acid will not cause any further change. The latter accounts for the flat portion of the curves in figure 1 of the present paper and in figure 1 of Pectin Studies I (7). It is apparent that anything that may change the rate of gelation will change the position of the optimum in any given system.

SUMMARY

A colloid theory to explain the process of pectin jelly formation is formulated. It is shown that it assists in explaining and to some extent anticipating the behavior of different types of pectin.

On the basis of this theory it is postulated that the so-called "optimum hydrogen-ion concentration" of jelly making may be varied by changes in time, the same as it is through changes in sugar concentration. Experimental data supporting this thesis are presented.

The effect of any substance added to a pectin jelly system which registers as a change in jelly strength of that system may be due to (a) an effect on the rate of gelation, or (b) an effect on the ultimate jelly structure, or (c) a combination of these two.

It is shown that apple pectin jellies rapidly prepared at 55°C. have abnormally high jelly strength as compared with jellies prepared by the short-boil method, indicating that only a fraction of the true jelly strength is obtained by the usual methods of preparing jellies.

Data presented show that the original amount of pectin is recoverable

unchanged from jellies prepared either at 50°C. or at 100°C. This proves that the difference in jelly strength is due not to pectin destruction at the higher temperatures but to structural differences in the pectin network forming the jelly. It is suggested that the amount of water bound by the precipitated pectin may differ depending upon the temperature at which the precipitation occurs.

Acknowledgment is due W. VanCamp and J. S. Kemp for assistance in the preparation of the jellies and in the determination of pH and jelly strengths.

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THE COMPRESSIBILITY COEFFICIENTS OF SOLUTIONS OF EIGHT ALKALI HALIDES

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Received November 9, 1933

Although the compressibility coefficients of aqueous solutions have been determined by several investigators,[1] there exist at present no comparable measurements of this property for a series of solutions of related substances. As a preliminary step to fill this need, the compressibility coefficients of a number of solutions for each of eight alkali halides have been determined at 35°C. over the pressure range 100 to 300 metric atmospheres (megabars). The solutions measured were prepared from purified materials; their composition and density were also measured with considerable precision.

PURIFICATION OF MATERIALS

The general reagents used in the purification of the salts may be described briefly. Water was doubly distilled, once from alkaline permanganate and then once from dilute sulfuric acid with the use of tin condensers. Constant boiling hydrochloric acid and hydrobromic acid were obtained by distillation through a quartz condenser.

The starting material for the preparation of lithium chloride and bromide was lithium carbonate of C.P. grade. The carbonate was first washed repeatedly with water until there was no test for halogen, and was then converted to the chloride or bromide by solution in the halogen acid. In order to precipitate any basic impurities a slight excess of carbonate was left at the end of the solution. After boiling the solution the residual carbonate was filtered off. The solution containing the halogen salt was then evaporated until a crop of crystals formed on cooling the solution in ice. These crystals were collected and were drained with the aid of a centrifuge. This crystallization operation was repeated until about two-thirds of the salt in solution was obtained in the form of crystals.

The sample of sodium chloride used was some left over from an atomic weight determination and was of a very high degree of purity. Pure sodium bromide was obtained by a single crystallization of the C.P. salt

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[1] Literature references to work before 1923 are given in the International Critical Tables, Vol. III, p. 439. Measurements reported since 1923 are given in references 1, 2, and 6.

from water with centrifugal drainage. Sodium iodide which had been synthesized from pure sodium oxalate and iodine was available from a previous research.

Potassium chloride was precipitated once from aqueous solution by conducting hydrogen chloride gas to the surface of the solution. Centrifugal drainage was used to separate the salt from the mother liquor. The potassium bromide and potassium iodide were purified in exactly the same manner as sodium bromide.

PREPARATION OF SOLUTIONS AND THEIR DENSITY DETERMINATIONS

One stock solution of lithium chloride and two of lithium bromide were prepared by dissolving the salts in an almost minimum amount of water. The halogen content of these solutions was found by precipitation with silver nitrate and weighing as the silver halide. The results of these analyses, which were carried out with great care, are given in table 1. The other solutions of these salts were prepared by dilution of weighed portions of these stock solutions.

TABLE 1

Analysis of lithium halide solutions

(All weights reduced to vacuum standard)

SOLUTION	WEIGHT OF SAMPLE	WEIGHT OF AgX	WEIGHT PER CENT OF LiX IN SOLUTION
	grams	*grams*	
LiCl	3.10328	4.41553	42.086
	3.16457	4.50251	42.084
			Av. = 42.085
LiBr (solution I)	3.36461	4.39467	60.410
	3.76652	4.91968	60.409
			Av. = 60.410
LiBr (solution II)	3.93692	4.66161	54.764
	3.92118	4.64256	54.759
			Av. = 54.761

The solutions of the sodium and potassium salts were prepared by dissolving a weighed amount of the salt in water and then determining the weight of the resulting solution. This procedure was adopted because, according to Baxter and Wallace (3), the sodium and potassium salts can be thoroughly dried without danger of decomposition. The two chlorides were fused in platinum vessels previous to weighing. The bromides and iodides, however, were heated in platinum only to 250°C. After two hours of heating these salts were powdered by gentle grinding in an agate mortar and the heating continued for another two-hour period. After a second grinding the salts were subjected to a final heating of at least three hours prior to weighing. It may be noted here that a few of the dilute solutions of these salts were prepared by dilution of weighed samples of the more concentrated solutions. These cases will be indicated in the table of results (table 3). Immediately after their preparation all the solutions were transferred to Pyrex glass-stoppered bottles. To prevent loss by evaporation during storage, each bottle was covered with a bottle cap held by a rubber collar which fitted tightly around the neck of the bottle.

The density flasks were ordinary 100-cc. graduated flasks, the necks of which had been constricted to about 3 mm. at the point of graduation to secure greater accuracy in setting the meniscus. The volumes of these flasks at 35°C. were found by dividing the vacuum weight of their water content by the density of water at that temperature (0.99406). To determine the density of a salt solution, the weight in vacuo of that amount of solution which filled a flask to the graduation was found and divided by the volume of the flask.

The following observations will complete the foregoing description of the preparation of the solutions and their density determinations. All weighings were made with calibrated weights on the same balance. Whenever flasks were involved, suitable counterpoises were employed. Precautions were always taken to insure that the surfaces of the flask and counterpoise were subjected to the same treatment. All weighings were reduced to vacuum standard by the usual formula. The thermostat employed in the density measurements was the same one used in the compressibility experiments and will be described in more detail later. To bring the density flask and its contents to the desired temperature the flask was immersed in the thermostat and allowed to remain there for at least two hours before the final adjustment of the meniscus. This adjustment was accomplished in two ways. If the composition of the solution had already been established, the adjustment was made by means of fine capillaries. In some instances, however, the weight of the solution in the density flask served also as the final weight in the determination of the composition of the solution by dilution. In these cases the meniscus was adjusted either by addition of water or by evaporation by passage of a current of dry filtered air over the surface of the meniscus.

Since the weight of a solution in the density flask was always greater than 100 g. and was determined to the nearest milligram, the precision of the density measurements is at least one part in 50,000. Check measurements were not made as a rule, but the occasional ones, using different flasks, agreed well within the above estimate. The flasks were again calibrated after being in use for a year and showed no appreciable change. The precision of the weight per cent composition of the solutions varies somewhat with the method of preparation and diminished with decreasing concentration. The uncertainty in this quantity is probably less than one part in 10,000.

THE DETERMINATION OF THE COMPRESSIBILITY COEFFICIENTS

These measurements were made by the method in use in the Harvard Laboratory. Since this method has been described fully in other papers (7), it will be necessary to give here only the more important details bearing on the present experiments.

The compression pump, which was manufactured by A. L. Henderer's Sons, was connected with the compression cylinder and the pressure gage. This gage was of the absolute type, in which pressures are measured by an oscillating piston weighted with carefully standardized weights. A piston with an accurately known area (0.31619 cm.^{2}) was loaned to us for this work. The piezometer was the one used by Dr. B. J. Mair and Miss E. H. Lanman in their experiments (5a). It was constructed of glass and was provided with a solid glass stopcock which was removed in order to fill the vessel. The piezometer had a volume of about 34 cc. and in an experiment it contained, as a rule, approximately 31 cc. of solution and 3 cc. of mercury.

The compression cylinder was mounted in a large thermostat which has already been described (9). It was possible to regulate the temperature of the bath so that the maximum variation was less than 0.005°C. The temperature of the bath was 35.00°C., established by means of a mercury thermometer certified by the Bureau of Standards.

The compressibility coefficients were calculated by use of the usual equation

$$\beta = \frac{(w_2 - w_1)D}{d \cdot 200 \cdot W} + \beta'$$

where

W is the weight of solution contained in the piezometer;

w_1 is the weight of mercury needed to compensate for the volume change produced by changing the pressure from 100 to 300 megabars when the piezometer is filled with mercury;

w_2 is the weight of mercury needed to compensate for the volume change produced by changing the pressure from 100 to 300 megabars when the solution is filled with W grams of solution and mercury;

D is the density of the solution at 35°C. and at atmospheric pressure;

d is the density of mercury at 35°C. under 300 metric atmospheres pressure (13.525);

β' is the compressibility coefficient of the reference substance, mercury, and was assumed to be 4.00×10^{-6}; and

β is the average compressibility coefficient over the pressure range 100 to 300 metric atmospheres of the substance in the piezometer.

In determining the values of w_1 and w_2 the following procedure suggested by Mair and Lanman was adopted. The amount of mercury in the piezometer was adjusted at the outset so that the electrical contact through the platinum wire–mercury interface was broken when the applied pressure was very close to 300 megabars. After the exact pressure was measured, mercury was removed from the piezometer until the pressure necessary to break the contact was approximately 100 megabars. Following exact determination of this second pressure, the mercury, which had been withdrawn and in the meantime weighed, was now returned to the piezometer and the initial pressure checked. The values of w_1 or w_2 corresponding to exactly 200 metric atmospheres were calculated by direct proportion from the weight of mercury removed and the pressure difference which covered very closely the range 100 to 300 megabars.

TABLE 2

Data and calculations for the compressibility coefficient of sodium iodide solution No. 4

	EXPERIMENT I	EXPERIMENT II
Weight of piezometer, mercury, and solution (grams)	134.386	134.324
Weight of piezometer and mercury (grams)	100.136	100.015
Weight of solution in air (grams)	34.250	34.309
Vacuum weight of solution (W) (grams)	34.282	34.341
Density of solution	1.10998	1.10998
Weight of mercury removed (grams)	3.2023	2.8964
High pressure point* (megabars)	306.32	292.09
Low pressure point (megabars)	95.38	101.71
Check high pressure point (megabars)	306.38	292.11
Accepted high pressure point (megabars)	306.35	292.10
w_2 (grams)	3.0358	3.0426
w_1 (grams)	0.1500	0.1500
$\beta \times 10^6$	38.54	38.56
Accepted value of $\beta \times 10^6$	38.55	

* Pressure in megabars equals $\frac{\text{weight on gage} \times \text{acceleration of gravity}}{\text{area of piston} \times 10^6}$ where weight on gage includes weight on platform plus weight of platform; acceleration of gravity is 979.272, and area of piston was 0.31619 cm².

Certain points with regard to the routine of the experiments should perhaps be noted here. Following the recommendation of Cohen and Schut (4), the capillary tube below the platinum contact was allowed to become moistened with water before the initial pressure application in each experiment. The practice was adopted of completing the pressure de-

TABLE 3

Table of results

SOLUTION	WEIGHT PER CENT OF SALT	DENSITY	$\beta \times 10^6$	AVERAGE DEVIATION
Lithium chloride solutions				
1 (ds)	42.031	1.26364	20.12	0.05
2 (ds)	34.898	1.20970	22.61	0.01
3 (ds)	26.021	1.14836	26.14	0.03
4 (ds)	23.010	1.12896	27.41	0.02
5 (ds)	18.969	1.10418	29.06	0.03
6 (ds)	16.279	1.08776	30.52	0.00
7 (ds)	9.6550	1.04943	34.45	0.01
8 (ds)	4.1221	1.01772	38.35	0.00
Lithium bromide solutions				
1 (i)	60.410	1.72090	22.37	0.02
2 (i)	54.761	1.60856	24.13	0.01
3 (d1)	49.949	1.52364	25.69	0.05
4 (d1)	45.438	1.45294	27.09	0.03
5 (d2)	43.493	1.42456	27.70	—
6 (d1)	36.696	1.33423	29.46	0.02
7 (d2)	31.897	1.27784	30.94	0.02
8 (d2)	25.388	1.20827	32.92	0.03
9 (d4)	17.229	1.13097	35.50	0.00
10 (d2)	12.959	1.09397	37.17	0.02
11 (d2)	8.6052	1.05845	38.57	0.01
Sodium chloride solutions				
1 (i)	24.8200	1.17942	27.10	0.01
2 (i)	16.9863	1.11690	30.99	0.03
3 (i)	9.1598	1.05852	35.56	0.01
4 (d1)	6.1298	1.03671	37.54	0.02
5 (d2)	2.8661	1.01388	39.71	0.03
Sodium bromide solutions				
1 (i)	49.295	1.54400	23.42	0.03
2 (i)	32.380	1.30294	29.74	0.03
3 (i)	20.7701	1.17443	34.03	0.00
4 (i)	9.8333	1.07392	38.10	0.02
Sodium iodide solutions				
1 (i)	60.802	1.80644	24.22	0.01
2 (d1)	40.413	1.42173	31.39	0.01
3 (d1)	22.712	1.19758	36.36	0.03
4 (d2)	13.896	1.10998	38.55	0.01

TABLE 3—*Concluded*

SOLUTION	WEIGHT PER CENT OF SALT	DENSITY	$\beta \times 10^6$	AVERAGE DEVIATION
Potassium chloride solutions				
1 (i)	26.522	1.17419	29.64	0.02
2 (i)	17.2876	1.10725	33.35	0.04
3 (i)	7.4440	1.04118	37.83	0.02
Potassium bromide solutions				
1 (i)	40.058	1.36525	29.51	0.01
2 (i)	32.576	1.27822	31.72	0.15
3 (i)	22.985	1.18086	34.68	0.04
4 (i)	10.452	1.07209	38.54	0.04
Potassium iodide solutions				
1 (i)	58.262	1.68149	27.74	0.16
2 (i)	34.901	1.32072	34.22	0.12
3 (i)	16.415	1.12576	38.44	0.17
4 (d2)	8.9594	1.06226	40.04	0.02
5 (d1)	4.4120	1.02648	40.87	0.04

termination fifteen minutes after the initial application of pressure. Further, in a pressure determination sufficient pressure was applied first to just break the electrical contact between the mercury in the piezometer and the platinum wire in the capillary. The pressure was then gradually reduced until contact was just made and the pressure corresponding to this point was the one accepted.

The value of the piezometer constant w_1 was found to be 0.1500 g. from eight different experiments made over a period of one year. Mair and Lanman found w_1 to be 0.1473 g. for the same piezometer at 25°C. The 2 per cent difference is a reasonable figure for the change in the compressibility of the glass and mercury for the 10°C. change in temperature.

In the table of results (table 3) will be given only the final calculated values of the compressibility coefficients for the solutions. To illustrate both the experimental procedure of the compressibility determination and the method of computation of the data, the calculations for a typical experiment are given in table 2.

RESULTS

All of the results of the experiments are summarized in table 3. Along with each solution number are given symbols to indicate the method of preparation of that solution. In this code "i" means that the solution was made independently of all other solutions while, for example, "d2" indicates that that solution was prepared by dilution of solution no. 2 of that series. With the exception of lithium bromide solution No. 5, each value of β is the mean of at least two independent measurements. In

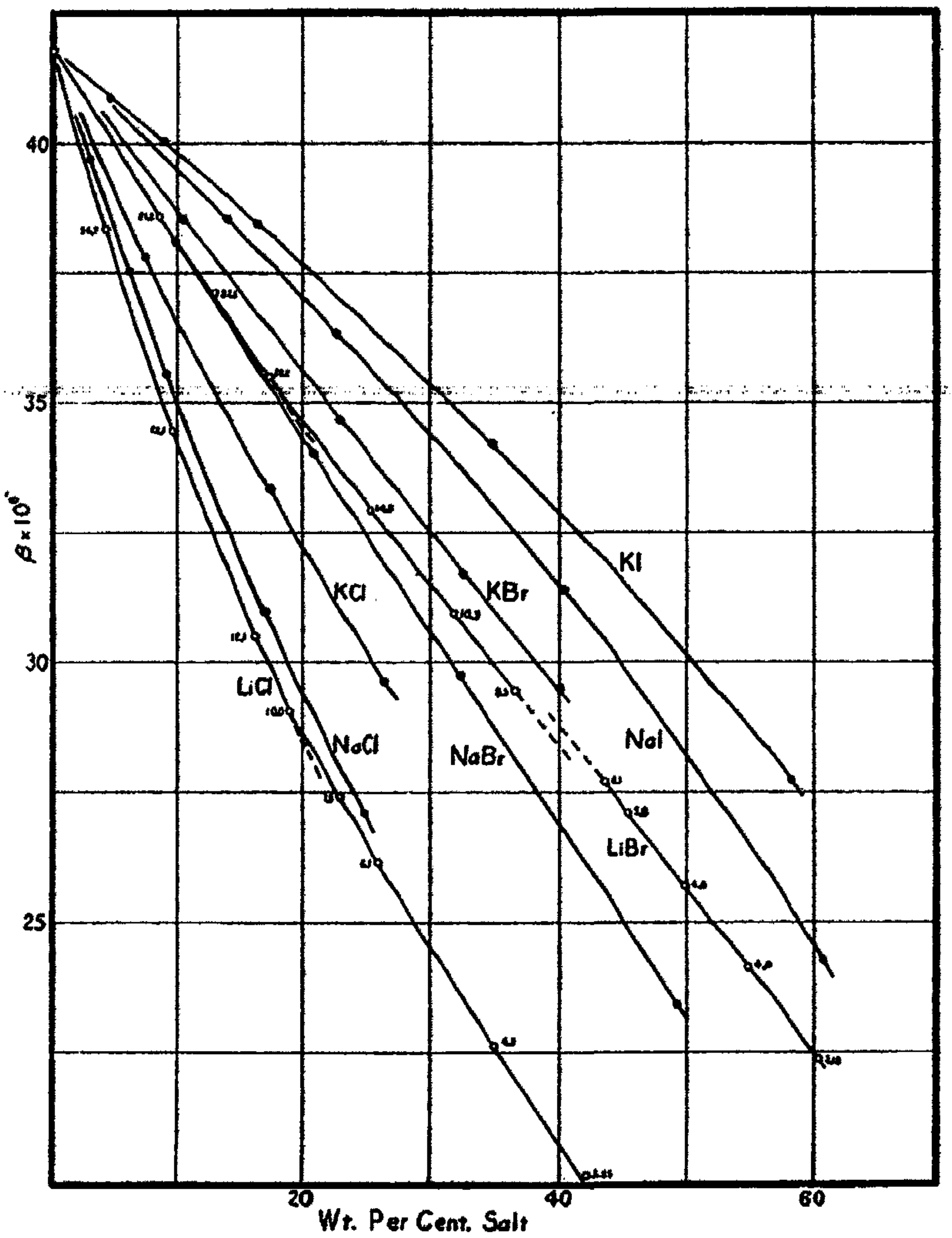

FIG. 1. THE COMPRESSIBILITY COEFFICIENTS OF SOLUTIONS PLOTTED AGAINST THE CONCENTRATION

order to have a rough measure of the uncertainty of the mean value of β there is given in the last column of table 3 the average deviation of the individual values of β from the given mean, expressed in the units of the compressibility coefficient. Attention is called to the fact that a number of improvements in both technique and apparatus were made in the course of the compressibility measurements of solutions of potassium bromide and potassium iodide and of lithium chloride solution No. 1, which were the first to be investigated. For this reason the β values of these solutions are not so precise as those of the other solutions, as is evident from the data in the last column.

Figure 1 is presented to show the nature of the variation of the compressibility coefficient with the composition of the solutions. It can be seen that the anion determines both the relative position and the shape of the curves drawn through the plotted points. Thus, the lines representing the chlorides are all convex upwards; the lines representing the iodides are all convex downwards; and the lines representing the intermediate bromides have been drawn straight. The solutions of the two lithium salts, however, exhibit some noteworthy anomalies. Since these anomalies are apparently associated with the molecular composition of the solutions, the number (N) of moles of water per mole of salt for the various solutions is given in the graph alongside the plotted points. In the case of the lithium chloride solutions there is a definite break in the variation of β with concentration at the solution with the composition $N = 10$. This critical point is the same as that found from the examination of such other properties of lithium chloride solutions as the density and magnetic susceptibility. As a matter of fact the investigation (8) of this last-named property indicated that the magnetic susceptibility of lithium chloride has two definite values, one in solutions less concentrated than $N = 10$, and the other in solutions more concentrated than $N = 6$. The transition between these two distinct values takes place in the concentration region $10 > N > 6$. Whether this second change in the solution state would affect the compressibility of the solutions cannot be ascertained from the present data. The possibility of a second break in the β-concentration curve at a point where $N = 6$ is not entirely out of the question, because the plotted point $N = 3.25$ does not fall on the curve as drawn.

Lithium bromide solutions appear to be more irregular even than those of lithium chloride. In the first place the compressibility coefficients of these solutions do not follow the usual sequence Li–Na–K. In the second place there are two abrupt changes in the variation of β with concentration. One of these breaks occurs in rather dilute solutions, somewhere in the concentration region $30 > N > 24$. The change in the rate of variation of β with percentage composition at this point is not very different from that found in the lithium chloride solutions. The second break in concentrated solutions $8 > N > 6$ is of an entirely different type. The rate of change of β with concentration does not appear to be affected by the change in the solution state, but the β values in the more concentrated solutions are 0.4×10^{-6} units higher than they would be if there were no break in the variation of β with concentration. Furthermore, this change in the solution state must take place in a rather short concentration range which we hope to explore more carefully. In conclusion it should be noted that Hüttig and Keller (5) found that the densities, refractive indices, and coefficients of extinction of the lithium halide solutions do show discontinuities with changes in concentration when $N = 6$, near 30, and 75.

Further discussion of these results from a different point of view will be the subject of another paper.

In conclusion we wish to express our gratitude to Professor Arthur B. Lamb of Harvard University for the loan of the piston of the pressure gage used in this investigation.

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THE MICRODETERMINATION OF VAPOR DENSITY

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Received March 2, 1934

In a recent research we had need of an apparatus for determining the vapor densities of a series of compounds which could be vaporized only under reduced pressure. Such determinations have been made in the past, but usually with a constant volume apparatus; the apparatus now described possesses features such as the simplicity of manipulation and the rapidity with which determinations are made which should commend it to anyone who is determining the vapor densities of substances which decompose on boiling at atmospheric pressures or substances available to the extent of only a few milligrams. The method is also useful for substances whose high boiling point renders the determination of their vapor density at ordinary pressures somewhat difficult.

The apparatus, shown in figure 1, consists of a vaporization tube, A, 1 meter in length and of 300-cc. capacity, closed with a well-fitting rubber bung and surrounded with a copper jacket, B. The latter is lagged with asbestos, fitted with a side-arm condenser, C, and is attached to the flask, D, in which the bath liquid is heated. The vaporization tube connects to two side tubes, one, on the left, containing a phial with a few milligrams of the substance under examination and a nail, which, when pulled by a magnet, ejects the phial into the vaporization tube. The other side tube leads to a manometer, E, containing a light liquid of low vapor pressure (ethyl phthalate or nitrobenzene), to one arm of a Hempel buret, F, containing clean, dry mercury, and to a tap, G, through which the apparatus was exhausted by means of a Cenco pump. The other arm of the Hempel buret was connected through a reservoir of 2-liters capacity, H, to stabilize the pressure to the tap, K, and thence to the common lead to the pump. Another tap, not shown in the diagram, enabled the pump to be cut off from the rest of the apparatus. All joints were sealed with Picein wax.

In practice it was found that, owing to minute traces of volatile material in the gauge liquid which could not be removed even by long heating *in vacuo*, the manometer, E, did not record absolute pressures. It was used, therefore, merely as a pressure indicator and a McLeod gauge, M, was incorporated in the system.

In making a determination the bath was heated until the liquid was refluxing well up the condenser arm, and the apparatus was exhausted with all the taps open until a pressure of 5 to 10 mm. of mercury was registered on the manometer, E, when the taps were closed. The phial was projected into the vaporization tube, its fall being broken by a small quantity of

5th

Fig

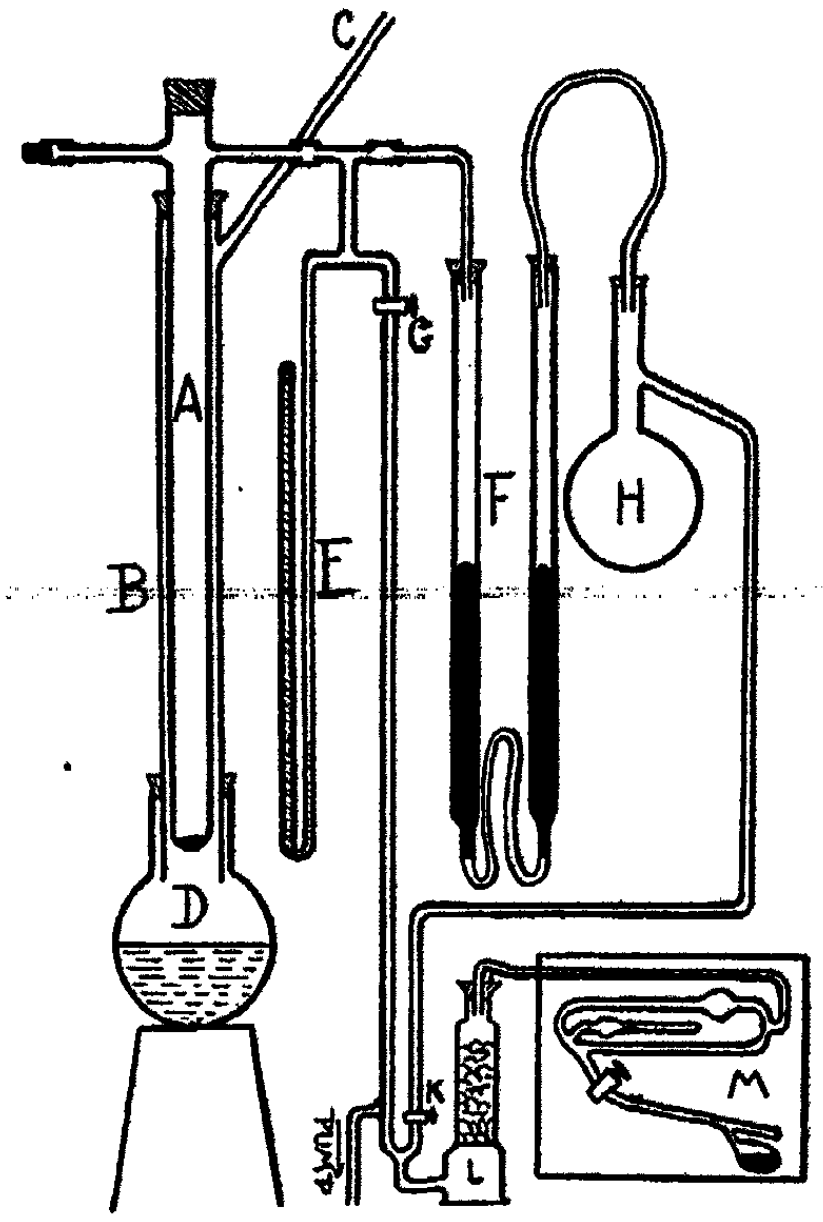

Fig. 1. Apparatus for Determination of Vapor Density under Reduced Pressure

TABLE 1

BATH LIQUID	TEMPERATURE	SUBSTANCE	QUANTITY USED	MOLECULAR WEIGHT (OBSD.)	MOLECULAR WEIGHT (CALCD.)
	degrees C.		*mg.*		
Nitrobenzene.........	211	Dibromobenzene	4	224	236
Nitrobenzene.........	211	Dibromobenzene	4	246	236
Nitrobenzene.........	211	Anthracene	5	182	178
Water................	100	Acetoacetic ester	5	128	130
Xylene...............	143	Carvone	5	146	150
α-Pinene.............	156	Geranyl acetate	7	206	196
α-Pinene.............	156	Geranyl acetate	6	201	196

fusible metal at the bottom of the tube (fusible metal is superior to glass wool, which is liable to evolve occluded gases under reduced pressure). Vaporization occurs in two minutes at the most, the gauge, E, being maintained at a constant level during the vaporization by lowering the right hand arm of the Hempel buret. When the vaporization was complete the taps G and K were opened, the gauge, E, restored to its original level by further slight evacuation, and the pressure recorded with the McLeod gauge. The calculation follows that of the ordinary Victor Meyer determination.

The method is superior to the constant volume method under reduced pressure since (1) it avoids the necessity for capillary tubing outside the heating jacket, and (2) it does not require a knowledge of the volume of the apparatus and the temperature of the jacket. One precaution must be mentioned. On admitting air at the conclusion of an experiment a film of moisture invariably condenses on the sides of the Hempel buret. This is revaporized during another experiment and causes a considerable error. It is necessary at the end of a determination to let the vacuum down with the mercury column fully raised and then to lower the column after re-evacuation and to warm the sides of the buret. The buret arms may be enclosed in water jackets at constant temperature.

Table 1 exemplifies some of the results obtained. The apparatus gives results correct to 3 to 5 per cent with ordinary precautions, an error which might easily be reduced to 1 to 2 per cent if so desired.

A DISCUSSION OF PATRICK AND ALLAN'S ARTICLE ON DIFFUSION OF ELECTROLYTES IN SILICA GEL

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Received July 18, 1934

In a recent article by Patrick and Allan (1), entitled "Diffusion of Electrolytes in Silica Gel," the authors in their discussion make the following statement: "According to the Nernst theory of diffusion, which leads to the elementary explanation of the liquid potential, a mobile ion should increase the rate of diffusion of a more slowly moving oppositely charged ion. Furthermore in the case of mixed electrolytes the more mobile ion will be retarded by the other ions, which in turn will experience an increase in mobility. This simple theory has been found to be in agreement with much experimental fact when dealing with ordinary diffusion phenomena. However, in the case of diffusion from a solution through a rigid gel structure, the above explanation no longer holds. Our washing of impregnated gels showed a marked retardation of the diffusion of the salt in the presence of acid, while our diffusion experiments through silica gel discs not only definitely proved the same point, but we were also able to show that the diffusion of the acid was speeded up in the presence of salt. These facts are in conflict with the Nernst theory; incidentally, Nernst never applied his ideas to systems such as used in this study."

The purpose of the present communication is to show that "these facts" are not only in qualitative, but also, in spite of the high concentrations of the electrolytes, in excellent quantitative agreement with Nernst's theory of diffusion of electrolytes.

In Patrick and Allan's diffusion experiments, one face of a cylinder of silica gel was in contact with a stirred aqueous solution of the electrolyte or electrolytes; the opposite face was bathed in a stream of pure water. After a steady state of diffusion had been reached, the authors measured the quantity of electrolyte which diffused through the gel in twenty-four hours. Assuming the concentration of electrolyte to fall off linearly in the silica gel, the authors were able to calculate the diffusion coefficient, knowing of course the cross-section and length of the cylinder of gel.

Consider a solution in which the concentrations (in moles per cm.^{3}) of sodium chloride and hydrogen chloride are C_1 and C_2, respectively. We assume the solutions to be so dilute that the osmotic pressures P_1, P_2, and

P_3 of sodium, hydrogen, and chloride ions are given by the equations $P_1 = C_1RT$, $P_2 = C_2RT$, $P_3 = CRT = (C_1 + C_2)RT$. Let u_1, u_2, and u_3 be respectively the velocities of the ions in centimeters per second when unit force (apart from the frictional force) acts on one mole of each kind of ion. On account of the differences in the numerical values of u_1, u_2, and u_3, the ions will be acted on by electric forces. We represent the potential of these forces by V expressed in such units that $-\frac{\mathrm{d}V}{\mathrm{d}X}$ is the electric force in the positive X-direction on one gram-equivalent of positive ions. It readily follows that the number of moles (S) diffusing per second through the constant cross-section q will be given for the three kinds of ions by the equations:

$$S_1 = -qu_1\left(\frac{\mathrm{d}P_1}{\mathrm{d}X} + C_1\frac{\mathrm{d}V}{\mathrm{d}X}\right) \text{ for Na}^+ \text{ ions}$$

$$S_2 = -qu_2\left(\frac{\mathrm{d}P_2}{\mathrm{d}X} + C_2\frac{\mathrm{d}V}{\mathrm{d}X}\right) \text{ for H}^+ \text{ ions}$$

$$S_3 = -qu_3\left(\frac{\mathrm{d}P_3}{\mathrm{d}X} - C_3\frac{\mathrm{d}V}{\mathrm{d}X}\right) \text{ for Cl}^- \text{ ions}$$

By means of the condition, $S_1 + S_2 = S_3$, we can eliminate $\frac{dV}{\mathrm{d}X}$ from these equations. On account of the linear fall in C_1 and C_2 through the gel, the ratio $\frac{C_2}{C_1} = r$ is constant throughout the cylinder and $\frac{\mathrm{d}C_2}{\mathrm{d}X} = r\frac{\mathrm{d}C_1}{\mathrm{d}X}$. Substituting for P_1 and P_2 the expressions C_1RT and C_2RT, respectively, we find

$$S_1 = -q\frac{2u_1u_3}{u_1+u_3}RT\frac{\mathrm{d}C_1}{\mathrm{d}X}\left[\frac{1+r}{1+\left(\frac{u_2+u_3}{u_1+u_3}\right)r}\right] \tag{1}$$

$$S_2 = -q\frac{2u_2u_3}{u_2+u_3}RT\frac{\mathrm{d}C_2}{\mathrm{d}X}\left[\frac{r+1}{r+\left(\frac{u_1+u_3}{u_2+u_3}\right)}\right] \tag{2}$$

Representing by D_{10} the diffusion coefficient of sodium chloride in the absence of hydrogen chloride, and by D_1 the diffusion coefficient when the ratio of hydrogen chloride to sodium chloride is r, we find from equation 1

$$D_1 = D_{10}\left[\frac{1+r}{1+\left(\frac{u_2+u_3}{u_1+u_3}\right)r}\right] \tag{3}$$

Similarly if D_{20} and D_2 are the diffusion coefficients of hydrogen chloride in the absence and in the presence of sodium chloride, respectively, we find from equation 2

$$D_2 = D_{20}\left[\frac{r+1}{r+\left(\frac{u_1+u_3}{u_2+u_3}\right)}\right] \tag{4}$$

Since u_1 (for Na$^+$) is less than u_2 (for H$^+$), it follows from equations 3 and 4 that

$$D_1 < D_{10} \tag{5}$$

$$D_2 > D_{20} \tag{6}$$

The expressions 5 and 6 are in qualitative agreement with the experimental results obtained by Patrick and Allan. Quantitatively we have

$$\frac{D_1}{D_{10}} = \frac{1+r}{1+\left(\frac{u_2+u_3}{u_1+u_3}\right)r} \tag{7}$$

$$\frac{D_2}{D_{20}} = \frac{r+1}{r+\left(\frac{u_1+u_3}{u_2+u_3}\right)} \tag{8}$$

We can test equations 7 and 8 by replacing u_1, u_2, and u_3 by the equivalent ionic conductances U_1, U_2, U_3. Some error will be introduced by taking for the equivalent ionic conductances their values at infinite dilution. From the values at 18°C. we find, using the appropriate temperature coefficients, the following equivalent ionic conductances at 32.5°C.; Li$^+$ $= 45.7$, Na$^+$ $= 58.5$, K$^+$ $= 84.5$, H$^+$ $= 387.0$, and Cl$^-$ $= 85.8$. We give in tables 1 and 2 the values of $\frac{D_1}{D_{10}}$ and $\frac{D_2}{D_{20}}$ obtained experimentally by Patrick and Allan and those calculated by equations 7 and 8.

ABSOLUTE VALUES OF THE DIFFUSION COEFFICIENTS

The absolute value of the diffusion coefficient in water of a single electrolyte (e.g., sodium chloride) is given according to Nernst by the equation

$$D_{\text{calcd.}} = \frac{2u_1u_3}{u_1+u_3}RT$$

$$= \frac{0.04485}{86400} \times \frac{273+t}{273+18}\,\frac{U_1U_3}{U_1+U_3}\ \text{cm.}^2 \text{ per second}$$

For the diffusion through silica gel, Patrick and Allan obtained the diffusion coefficient from the equation

$$S_t = qD\frac{dC_t}{dX}$$

where S_t is the number of moles (e.g., of sodium chloride) diffusing per second and q is the cross-section of the gel. We give in table 3 the values of $D_{\text{obsd.}}$ (obtained by Patrick and Allan) and the values of $D_{\text{calcd.}}$ (calculated on the Nernst theory for diffusion in water).

TABLE 1

Observed and calculated values of the relative diffusion coefficient

Salt, 0.90 N; HCl, 1.15 N; r = 1.28; t = 32.5°C.

SALT	$\frac{D_t}{D_{10}}$		$\frac{D_t}{D_{20}}$	
	Observed	Calculated	Observed	Calculated
LiCl	0.41	0.41	1.43	1.46
NaCl	0.41	0.44	1.50	1.44
KCl	0.44	0.50	1.45	1.39

TABLE 2

Observed and calculated values of the relative diffusion coefficient

Salt, 1.80 N; HCl, 1.15 N; r = 0.64; t = 32.5°C.

SALT	$\frac{D_t}{D_{20}}$	
	Observed	Calculated
LiCl	1.79	1.78
NaCl	1.91	1.73
KCl	1.80	1.64

TABLE 3

Observed and calculated values of the diffusion coefficient

SALT	ORIGINAL CONCENTRATION	$D_{\text{obsd.}}$	$D_{\text{calcd.}}$	$\frac{D_{\text{calcd.}}}{D_{\text{obsd.}}}$
LiCl	0.90	1.92×10^{-6}	1.62×10^{-5}	8.4
NaCl	0.90	3.43×10^{-6}	1.90×10^{-5}	5.5
KCl	0.90	4.69×10^{-6}	2.32×10^{-5}	5.0
HCl	1.15	8.52×10^{-6}	3.83×10^{-5}	4.5

A possible explanation of the values given in the last column of table 3 can be furnished by supposing that the water in the gel through which the ions diffuse occupies a fairly definite fraction of the apparent volume of the gel. In other words, as a diffusion medium the cylinder of gel is equivalent to a cylinder of water of the same length but of much smaller cross-section,—about one-fifth to judge from the experiments with sodium chloride, potassium chloride, and hydrogen chloride, and about one-eighth when lithium chloride is used. The differences among the values of the last column of table 3 are too large to be attributed to experimental errors only; our picture of the state of a salt solution present in the gel is probably too much simplified.

In conclusion, I think it can be said that the diffusion of electrolytes in silica gel seems to take place in essentially the same way as in water and that in both cases the Nernst theory of diffusion of electrolytes is quantitatively applicable.

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THE APPARENT VOLUMES OF SALTS IN SOLUTION AND THEIR COMPRESSIBILITIES

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Received November 9, 1933

In recent years there has been a marked revival of interest in the problem of the volume changes that occur when a solution undergoes a change in concentration. An important factor in this was the discovery by Masson (11), and independently by Geffcken (4), of a simple relationship between the apparent molal volume of the solute and the concentration of the solution. As an outgrowth of previous studies (16, 17) of this empirical rule of Masson, the question of the effect of pressure on the apparent volumes appeared to be of considerable interest and significance. This question is the subject of the present paper. Because the existing compressibility data were considered to be too fragmentary for a satisfactory treatment of this problem, systematic measurements of the compressibility coefficients of solutions of the alkali halides were undertaken. The results of the first series of these experiments have already been reported (20) and will be used exclusively in this study.

The apparent molal volume (ϕ) of a solute is defined as

$$\phi = V - n_1 V_1 \tag{1}$$

where V is the volume of solution containing 1 gram-mole of solute, V_1 is the volume of 1 gram-mole of pure water at the temperature of the solution, and n_1 is the number of moles of water present in the solution. The compressibility of the apparent molal volume, which will be designated as $\bar{B}$ and which may be termed the apparent molal compressibility of the solute, is defined by the expression:

$$\bar{B} = -\frac{\partial \phi}{\partial P} = V\beta - n_1 V_1 \beta_1 \tag{2}$$

where $\beta \left[= -\frac{1}{V}\frac{\partial V}{\partial P} \right]$ is the compressibility coefficient of the solution and β_1 is that of water.

Masson's empirical rule for strong electrolytes may be expressed as follows:

$$\phi = kc^{\frac{1}{2}} + \phi^0 \tag{3}$$

Here k and ϕ^0 are constants characteristic of each electrolyte and temperature, and c is the concentration expressed in moles per liter. Since this equation[1] is the basis of the present inductive study, a brief review of its status will not be out of place. The applicability of this relationship was tested originally by Masson for a number of salts of diverse valence types. Subsequent more systematic tests (5, 15, 16) have covered the salts of the alkali halides and the alkaline earth halides. In general, these tests have all tended to confirm the validity of the empirical rule with the following qualifications. Equation 3 does not hold in extremely concentrated solutions of certain salts, such as the lithium halides, where chemical hydration is supposed to be a disturbing factor. Further, the above-named tests have been limited in scope to solutions more concentrated than 1 molar. In solutions less concentrated than this the ϕ values are too uncertain, because of the tremendous magnification of the experimental error involved in their calculation, to permit of a conclusive test. Within the past year, however, Geffcken (6, 7) and his coworkers have improved the technique for making the extremely precise density measurements which are essential for the calculation of accurate values of ϕ in very dilute solutions. Although not all of their measurements have been published, the results that are available may be summarized briefly as follows. With solutions of sodium bromide and ammonium nitrate at 25°C., equation 3 appears to be valid over the concentration ranges, 0.02 M to 5.5 M and 0.05 M to 7.5 M, respectively. In the case of sodium chloride solutions a break in the $\phi - c^{\frac{1}{2}}$ plot occurs at about 0.4 M. Solutions of sodium carbonate, although apparently normal at high concentrations, are quite irregular in concentrations less than 0.1 M. The abnormality consists not only in a deviation from Masson's rule, but in the most extreme dilutions the apparent molal volume begins to increase with decreasing concentration. These various tests may be summarized by stating that there is no reason to question the applicability of equation 3 to concentrated solutions of strong electrolytes, but that an uncertainty still exists regarding its general validity in dilute solutions. In this connection it may be mentioned also that Redlich and Rösenfeld (13) have given a derivation of equation 3 based on the Debye-Hückel theory and thermodynamics according to which the constant k has the same value for all electrolytes of the same valence type. In order to reconcile the actual data with their theoretical equations, they conclude that the latter hold only in very dilute solutions and that in concentrated solution the variation of ϕ with $c^{\frac{1}{2}}$ is not linear. Since some non-electrolytes also agree with Masson's rule, the significance of conclusions based upon the Debye-Hückel theory is open to question (9) because such

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[1] A review of this equation and of the similar expressions for the apparent heat capacity and apparent compressibility has been published recently by Gucker (9).

substances would not have the ion atmosphere which is a basic postulate of the theory.

From Masson's equation a relationship between the apparent molal compressibility $\bar{B}$ and concentration can be derived directly. If we differentiate equation 3 with respect to pressure, we get

$$\frac{\partial\phi}{\partial P} = \frac{\partial k}{\partial P}c^{\frac{1}{2}} + k\frac{\partial c^{\frac{1}{2}}}{\partial P} + \frac{\partial\phi^0}{\partial P} \tag{4a}$$

Since $c = 1000/V$, it follows that

$$\frac{\partial c^{\frac{1}{2}}}{\partial P} = -\frac{1}{2}\frac{c^{\frac{1}{2}}}{V}\frac{\partial V}{\partial P} = \frac{1}{2}\beta c^{\frac{1}{2}} \tag{4b}$$

where β is the compressibility coefficient of the solution. Now, if we let $f = \frac{1}{2}k\beta c^{\frac{1}{2}}$ and if, in accordance with equation 2, we designate $-\frac{\partial\phi}{\partial P}$ and $-\frac{\partial\phi^0}{\partial P}$ by $\bar{B}$ and $\bar{B}^0$, respectively, equation 4a can be written as:

$$\bar{B} + f = -\frac{\partial k}{\partial P}c^{\frac{1}{2}} + \bar{B}^0 \tag{5}$$

This equation will form the basis of much of our subsequent discussion. It can be tested most conveniently in the form written, as a linear relationship between $(\bar{B} + f)$ and $c^{\frac{1}{2}}$, which quantities can be calculated from experimental data. A plot of these variables will be presented later and from it the terms $-\frac{\partial k}{\partial P}$ and $\bar{B}^0$ can be derived directly.

Since our measurements designed to test equation 5 were initiated, relationships involving $\bar{B}$ or closely related factors have been proposed by two investigators. Adams (1), from his compressibility measurements of several sodium chloride solutions over a wide pressure range, calculated the fictive or partial compressibility of the solution which, for an infinitely dilute solution, is the same as the apparent compressibility. In a later paper Adams (2) stated that the specific apparent compressibility of the same solute could be represented by a linear function of the square root of the mole or mass ratio. Such a function implies that Masson's relation holds also "if the mole ratio or mass ratio is substituted for the volume concentration." A study of the properties of the apparent molal compressibility of solutes in solution has been published recently by Gucker (10), who recalculated for this purpose most of the available data. His conclusion was that $\bar{B}$ is a "linear function of $c^{\frac{1}{2}}$ over a wide range of concentration, temperature, and pressure." In a subsequent article (9) he showed that this relationship could be derived from the Debye-Hückel theory of solu-

TABLE 1

Values of the various solution factors at 35°C.

c	c_{300}	ϕ	ϕ_{300}	$-\bar{B}$	f
		Lithium chloride solutions			
0.9895	0.9971	18.60	19.06	27.09	0.21
2.3900	2.4065	19.30	19.75	22.69	0.29
4.1767	4.2024	20.08	20.45	18.62	0.34
4.9401	4.9690	20.22	20.57	17.34	
6.1272	6.1609	20.50	20.79	14.91	
7.0479	7.0849	20.62	20.89	13.90	
8.0654		20.74			
9.9576	10.0028	20.86	21.07	10.55	
12.5274	12.5780	21.00	21.17	8.83	
		Lithium bromide solutions			
1.0486	1.0568	25.61	26.01	20.00	0.14
1.6322	1.6444	25.80	26.15	17.58	0.16
2.2444	2.2605	26.01	26.35	17.20	0.18
3.5318	3.5552	26.36	26.64	14.13	0.22
4.6927	4.7219	26.54	26.78	12.05	0.23
5.6371	5.6705	26.67	26.88	10.74	0.24
7.1335	7.1732	26.62	26.79	8.62	0.25
7.6009	7.6423	26.64	26.80	8.07	
8.7621	8.8074	26.58	26.73	7.27	
10.1416	10.1908	26.42	26.55	6.38	
11.9692	12.0230	26.29	26.39	5.25	
		Sodium chloride solutions			
0.4971	0.5011	18.71	19.39	34.22	0.21
1.0872	1.0954	19.33	19.95	31.10	0.29
1.6571	1.6690	19.67	20.26	29.44	0.34
3.2457	3.2659	20.73	21.22	24.65	0.41
5.0080	5.0353	21.57	21.98	20.34	0.44
		Sodium bromide solutions			
1.0256	1.0335	26.19	26.69	25.10	0.27
2.3703	2.3865	26.88	27.28	21.50	0.28
4.0994	4.1240	27.73	28.09	17.80	0.33
7.3957	7.4305	28.72	28.98	12.84	0.34
		Sodium iodide solutions			
1.0287	1.0368	37.47	37.79	15.93	0.17
1.8141	1.8274	37.97	38.25	14.14	0.21
3.8322	3.8565	38.56	38.78	11.04	0.26
7.3258	7.3615	39.27	39.42	7.50	0.28

TABLE 1—(*Concluded*)

c	c_{300}	ϕ	ϕ_{300}	$-\bar{B}$	f
Potassium chloride solutions					
1.0397	1.0476	29.40	29.92	25.90	0.36
2.5671	2.5758	30.65	31.05	20.11	0.50
4.1769	4.2018	31.62	31.94	15.90	0.52
Potassium bromide solutions					
0.4591	0.4628	35.87	36.43	27.70	0.21
0.9416	0.9489	36.35	36.74	19.43	0.29
2.2806	2.2964	37.32	37.63	15.62	0.41
3.4987	3.5210	38.02	38.28	12.92	0.46
4.5951	4.6224	38.47	38.68	10.67	0.49
Potassium iodide solutions					
0.2728	0.2750	47.47	47.76	14.29	0.13
0.5732	0.5779	47.34	47.56	10.92	0.19
1.1131	1.1217	47.93	48.13	10.15	0.25
2.7763	2.7954	48.65	48.79	6.96	0.36
5.9006	5.9335	49.80	49.86	3.00	0.42

tion in conjunction with certain thermodynamic relationships. The only difference between Gucker's equation and our equation 5 is the factor f. The magnitude of this factor and its variation with concentration are such that it would be futile to attempt to prove one equation to be more nearly correct than the other without more precise compressibility data than those obtainable at present. We shall therefore make no attempt to compare the two expressions in this paper. Nevertheless, since both equations are empirical, there would seem to be an advantage in choosing to work with the one (equation 5) which is mathematically consistent with the fairly well established empirical rule of Masson. Furthermore, the term $(\bar{B} + f)$ may be regarded as a simpler concept than the calculated quantity $\bar{B}$, which involves concentration as a dependent variable. Application of pressure to a solution produces an increase in concentration which, in turn, would result normally in an increase in ϕ. This small increase in ϕ is one of the pressure effects included in the quantity $\bar{B}$. Since, however, it is equal to

$$f = k\frac{\partial c^{\frac{1}{2}}}{\partial P} = \frac{\Delta\phi}{\Delta P}$$

when k, ϕ^0 are constant, the term $(\bar{B} + f)$ represents the change in ϕ with pressure when the concentration is considered an independent variable.

Before describing the calculations of the various quantities which we shall require in our test of equation 5, there is a question of procedure that should first be pointed out. Since these quantities are all functions of pressure it is obviously desirable that they refer to the solution system under the same pressure. This condition cannot be fulfilled exactly by the use of our data because the compressibility coefficient measured is for a system under a pressure of 200 metric atmospheres, whereas the density data are for solutions under only atmospheric pressure. The error introduced by this discrepancy can be reduced to a negligible magnitude if all the quantities are calculated to apply to a system under the higher pressure, a fact which will be evident from the following description of the calculations of the quantities in question.

All the factors which we shall need in this study are assembled in table 1 and were calculated from the data for solutions at 35°C., given in the article already referred to. Certain symbols which will be employed may be defined at the outset:

% = percentage by weight of solute in solution.

M = gram-molecular weight of solute.

d, d_1 = densities of solution and pure water.

β, β_1 = average compressibility coefficients of solution and water at 200 megabars (or metric atmospheres) pressure. For the sake of brevity we shall refer hereafter to the pressure units simply as "atmospheres."

c = concentration in gram-moles of solute per liter of solution.

$$c = \frac{\% \cdot d}{M} \cdot 10$$

The precision of the calculated values of c is better than 0.02 parts per thousand. Values of c are given in the first column of table 1.

c_{200} = concentration of the solution under a pressure of 200 megabars. This quantity was also calculated by means of the above formula, using the density of the solution at 200 atmospheres. This density was computed by taking

$$d_{200} = d(1 + 200\beta)$$

This correction is, to be sure, only a first approximation, because the compressibility coefficient used does not give the change in volume over the pressure range 0 to 200 but gives the rate of change when the system is under a pressure of 200 metric atmospheres. A further correction to take this fact into account would be of the second order and would be negligible. Values of c_{200} are given in the second column of table 1.

ϕ = the apparent molal volume at atmospheric pressure expressed in cubic centimeters.

$$\phi = \frac{M}{\%d \cdot 10} - \frac{(100 - \%) \cdot M \cdot 1000}{\%d_1}$$

Since ϕ is a difference between two terms, its precision is very much less than that of the experimentally determined quantities and decreases rapidly with decreasing concentration. While in concentrated solutions the uncertainty is about 0.02 cc., in a 1 molal solution it may be 0.1 cc. or even slightly greater. Values of ϕ are given in the third column of table 1.

ϕ_{200} = the apparent molal volume at 200 atmospheres pressure, expressed in cubic centimeters. The calculation of these quantities is the same as that just described with the difference that the densities were corrected to the higher pressure by the formula given in the paragraph under c_{200}. In practice this density correction is most conveniently accomplished by subtracting 200 × $\bar{B}$ (see next paragraph) from the corresponding ϕ values. The error introduced by this approximation into the calculated values of ϕ_{200} is less than the uncertainties of the ϕ values. Values of ϕ_{200} are given in the fourth column of table 1.

$\bar{B}$ = apparent molal compressibility at 200 atmospheres pressure expressed in cc. atm.$^{-1}$ × 10^4.

$$\bar{B} = \frac{M\beta}{\%d \cdot 10} - \frac{(100 - \%)M \cdot \beta_1 \cdot 1000}{\%d_1}$$

Attention is called to the fact that no correction for the change in density with pressure has been made, as was necessary in the calculation of the ϕ_{200} values. The reason for this is that the compressibility actually measured is not the ideal coefficient but the average coefficient over the pressure range 100 to 300 metric atmospheres and is calculated from the following measured quantities:

$$\beta = -\frac{1}{V_0}\frac{\Delta V}{200}$$

Here ΔV refers to 200 atmospheres, but the V_0 is the volume at 1 atmosphere pressure. While the value of this last term at 200 atmospheres pressure could be computed approximately, the correction applied would be cancelled by the correction that would then have to be applied to d_s and d_1 in calculating $\bar{B}$. In short, by not correcting either V_0 or the densities we get $\bar{B}$ at 200 megabars pressure without any qualification. Since we shall not be able to use values of $\bar{B}$ at atmospheric pressure, we shall omit a designative subscript. With regard to the precision of these computed $\bar{B}$ values only the general statement can be made that they are the least precise quantities which we shall employ. As in the case of the apparent molal volumes, the uncertainty in $\bar{B}$ increases with decreasing concentration. Using sodium chloride solutions as an example, the uncertainty in the $\bar{B}$ value of the most concentrated solution is probably only two units in the second decimal, whereas in the 1 molal solution the uncertainty may amount to at least one unit in the first decimal. Values of $\bar{B}$ are given in the fifth column of table 1.

f = correction factor already defined (equation 5) as $\frac{1}{2}\beta kc^{\frac{1}{2}}$ and is expressed in the same units as $\bar{B}$. Both the $c^{\frac{1}{2}}$ and the k values used in these calculations were for systems under a pressure of 200 atmospheres. The k values used are given in table 2. Values of f are given in the sixth column of table 1.

In view of the fact that the values of $\bar{B}$ are known only for systems under 200 atmospheres pressure and that therefore our examination of equation 5 is limited to such systems, we are obliged to consider first the question of the validity of Masson's equation for systems under pressure. As a preliminary basis for the consideration of this question ϕ and ϕ_{200} have been plotted (figure 1) against $c^{\frac{1}{2}}$ and $c^{\frac{1}{2}}_{200}$, respectively. The values of the Masson constants as found from the drawn lines in the graph are given in table 2.

Concerning the $\phi - c^{\frac{1}{2}}$ plots for systems under atmospheric pressure, only a few observations are needed. The deviations of the plotted points from the drawn straight lines are less than the estimated uncertainties of the plotted quantities. The Masson constants for some of the solutions under consideration have also been determined by Geffcken (5) and, for the sake of comparison, are given in parentheses in table 2. There is excellent agreement between the two sets of constants except in the case of the potassium bromide solutions. The deviation from the linear relationship which is very evident in the concentrated solutions of the two lithium salts has been noted previously at other temperatures. The concentration at which the linear relationship breaks down is a matter of some interest. Masson's conclusion that the limit with lithium chloride solutions is a solution with the composition LiCl + $10H_2O$ is confirmed by our data ($c^{\frac{1}{2}}$ =

2.04). The limit for the lithium bromide solutions cannot be established so clearly. The limiting solution of this salt contains 24 to 30 moles of water per mole of salt. In the more concentrated solutions of these lithium salts ϕ appears to be a linear function of the number of moles of water present. This question we intend to treat in a separate note.

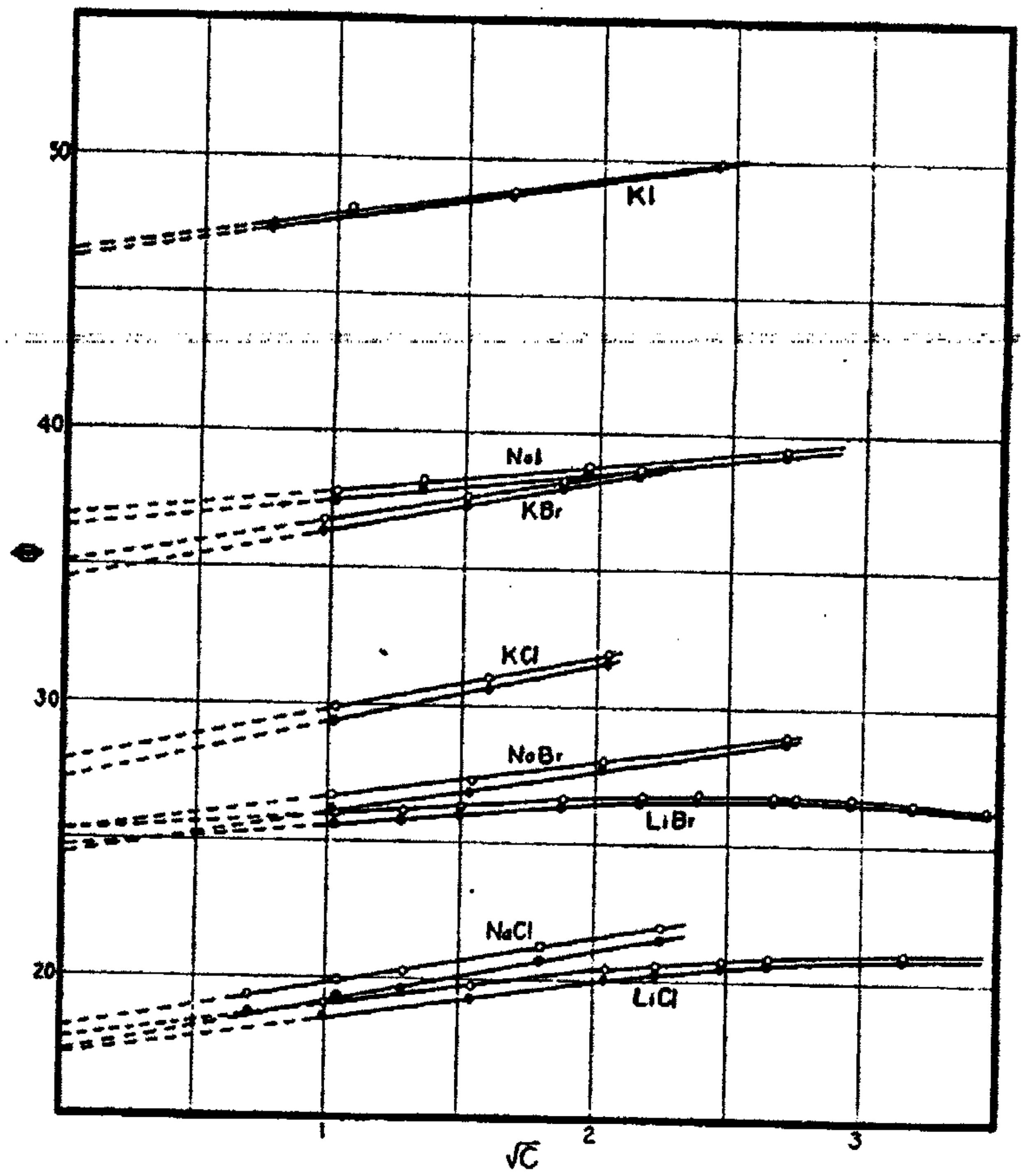

Fig. 1. Apparent Molal Volumes Plotted Against the Square Root of the Concentration when the Solutions Are under Atmospheric Pressure (Open Circles) and under a Pressure of Two Hundred Metric Atmospheres (Solid Dots)

We shall look upon the $\phi - c^{\frac{1}{2}}$ plots for solutions under pressure as a means of testing Masson's empirical equation for solutions under conditions entirely different from those for which the equation has previously been shown to hold. So far as can be judged from an inspection of the graph, the linear relationship holds as well for solutions under pressure as for solutions at atmospheric pressure. Further evidence supporting this tentative conclusion will be presented in the discussion of the next figure. We shall have occasion to use the constants (table 2) of the drawn lines later. The value of k_{200} has already been employed in computing the factor f (table 1). Attention should perhaps be called to the fact that increase in pressure results in an increase in ϕ^0 and a decrease in k. The only check on the present figures is with the ϕ values of sodium chloride solutions. The difference between ϕ_{200} and ϕ here is essentially the same as that (0.85 cc.) found by Adams (1) for the corresponding change in the partial molal volumes of this salt, which in infinite dilution become identical with the apparent molal volumes.

TABLE 2

Values of constants obtained from figure 1

SALT	ϕ^0	ϕ^0_{200}	k	k_{200}
LiCl	17.10	17.80	1.45	1.25
LiBr	24.75	25.35	0.75	0.65
NaCl	17.25 (17.25)	18.15	1.90 (1.92)	1.70
NaBr	24.45 (24.45)	25.31	1.55 (1.55)	1.34
NaI	36.45	36.85	1.08	0.97
KCl	27.22 (27.22)	27.90	2.13 (2.2)	2.00
KBr	34.55 (34.27)	35.15	1.85 (1.90)	1.65
KI	46.25 (46.25)	46.50	1.45 (1.42)	1.40

In concluding our discussion of figure 1 it may be noted that the drawn lines are extended only to the concentration of the saturated solutions. For solutions at atmospheric pressure the necessary data were obtained from the measurements of Scott and Durham (18). The limits of the lines for solutions under pressure were determined by plotting the estimated value of ϕ_{200}, which was computed by the method already described from the ϕ value of the saturated solution at atmospheric pressure as read from the graph. In this procedure no allowance is made for the change in solubility of the salt with pressure, which would be negligible for the small change in pressure involved.

In figure 2, values of $(\bar{B} + f) \times 10^4$ are shown plotted against values of $c^{\frac{1}{2}}_{200}$. From the fact that the plotted points fall so closely on the drawn straight lines it may be concluded reasonably that the relationship between $(\bar{B} + f)$ and $c^{\frac{1}{2}}$ is linear within the limits of error of the quantities involved. Since this conclusion is in agreement with equation 5, which was derived from Masson's equation, we have here additional evidence of the appli-

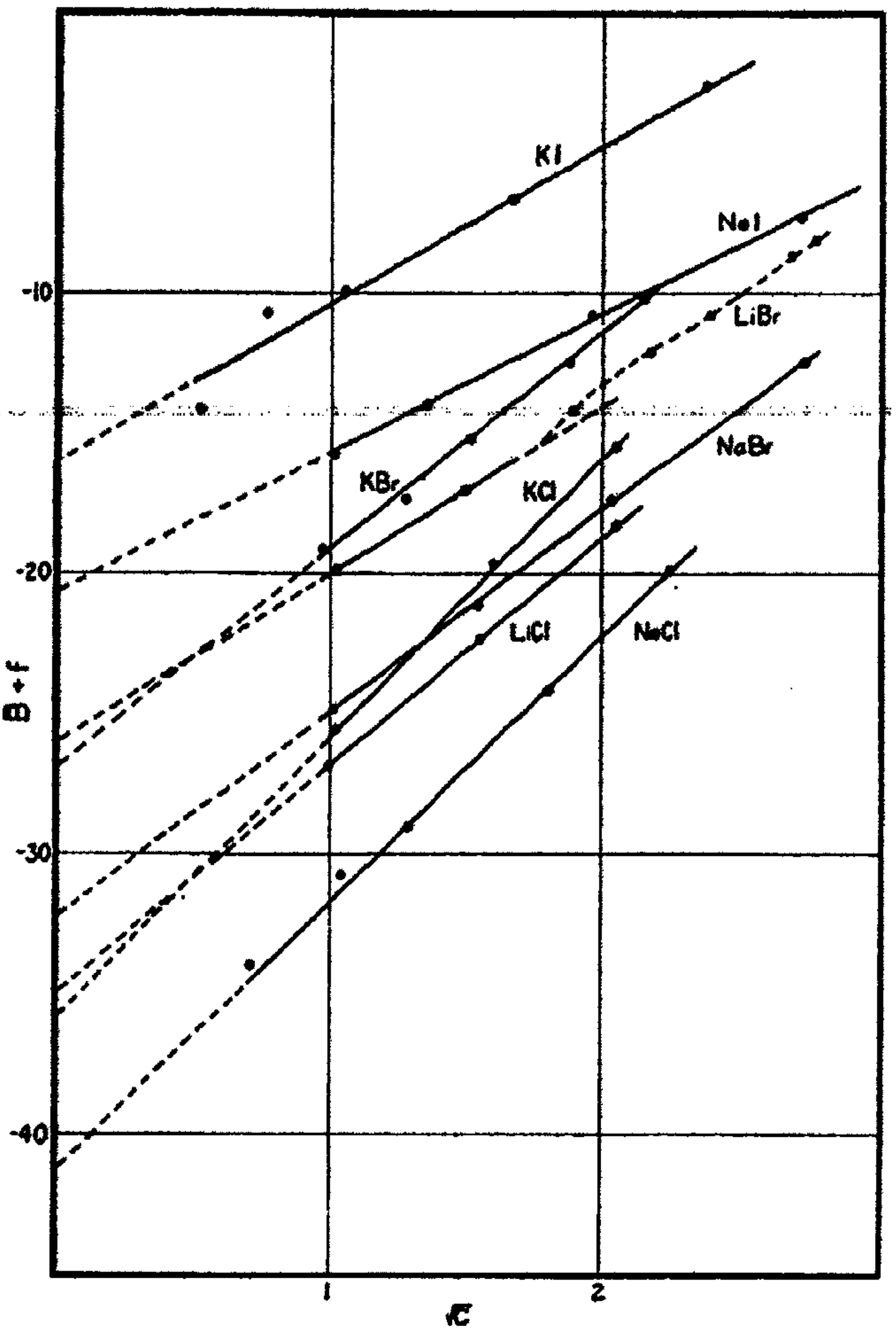

Fig. 2. Plot Showing the Linear Relationship between the Apparent Compressibility Factor $(\bar{B} + f)$ and the Square Root of the Concentration

cability of this empirical rule to solution systems under pressure. As a matter of fact, since this method of testing the basic equation is a great deal more sensitive to error than the $\phi - c^{\frac{1}{2}}$ plot, its outcome is especially valuable because it answers, so far as is possible at this time, the question of the validity of Masson's equation for systems under pressure.

The drawn lines have been extrapolated to values of $c = 0$. The corresponding values of $\bar{B}^0$ are given in table 3. These $\bar{B}^0$ values presumably represent simply the apparent compressibilities of individual ions, and consequently they might be expected to be the sum of the values characteristic of the component ions. That they are practically additive can be seen from the summary in table 4 of the differences between various combinations. The differences involving $\bar{B}^0$ of potassium iodide deviate slightly from the other corresponding differences; this is probably due to the greater uncertainty of the data of these solutions.

TABLE 3

Data bearing on the constants of equation 5

SALT	$-\bar{B}^0 \times 10^4$	$\frac{-dk}{dP} \times 10^4$	$\frac{-d(\ln k_{30})}{dP} \times 10^4$	$\frac{-d(\ln k_{30})}{dP} \times 10^4$ CALCULATED
NaCl	41.20	9.50	5.58	5.71
NaBr	32.20	7.30	5.45	5.37
NaI	20.60	4.95	5.11	4.53
KCl	35.80	10.00	5.00	5.12
KBr	26.90	7.75	4.70	4.69
KI	16.00	5.65	4.03	3.94
LiCl	34.90	8.05	6.43	(6.07)
LiBr	26.00	5.99	9.22	(5.69)

TABLE 4

The differences between various combinations

M	$\bar{B}^0_{MCl} - \bar{B}^0_{MBr}$	$\bar{B}^0_{MBr} - \bar{B}^0_{MI}$	X	$\bar{B}^0_{NaX} - \bar{B}^0_{LiX}$	$\bar{B}^0_{KX} - \bar{B}^0_{NaX}$
Li	(8.9)		Cl	6.3	5.4
Na	9.0	11.6	Br	(6.2)	5.3
K	8.9	10.9	I		4.6

With the exception of the two lithium salts the upper limit of the drawn lines is the concentration corresponding to the saturated state as found in figure 1. The upper limit of the lines representing the solutions of lithium salts is the assumed limit of the applicability of Masson's equation. In the case of the lithium bromide solutions, the dotted line represents the variation of $\bar{B}$ with $c^{\frac{1}{2}}$ over the concentration region where f might be taken as zero since k (figure 1) is here approximately zero.

The slopes of the drawn lines are given in column 3 of table 3 and according to equation 5 are equal to $-\frac{\partial k}{\partial P}$ at 200 atmospheres pressure. The values of this constant are very nearly the same for sodium and potassium salts with a common anion, a fact which suggests that the effect of pressure on k is determined largely by the nature of the anion. The ratio $(-\frac{\partial k}{\partial P}/k)_{200}$ is equal to $-\frac{\partial \ln k_{200}}{\partial P}$ and is also given in table 2.

A rough check of the values of $\bar{B}^0$ and $-\frac{\partial k_{200}}{\partial P}$ can be found in an examination of the Masson constants given in table 2. If $\bar{B}^0$ is taken to be the average decrease in ϕ over the pressure range, 1 to 200 atmospheres, then $200\bar{B}^0$ should give approximately the difference $\phi^0 - \phi^0_{200}$. Similarly, the approximate difference $k - k_{200}$ can be calculated from the values of $\frac{\partial k_{200}}{\partial P}$. The average difference between $\phi^0 - \phi^0_{200}$ and $200\bar{B}^0$ is only 0.07 cc., and the average difference between $k - k_{200}$ and $200\frac{\partial k}{\partial P}$ amounts to a little less than 0.04 unit.

Before we take up the interpretation of the various properties of solutions which we have been able to derive from our data, it is desirable to consider first the derivation of an expression giving the compressibility coefficient of solutions, β, as a function of concentration. According to equations 1 and 3 we can write

$$\phi = V - n_1V_1 = kc^{\frac{1}{2}} + \phi^0$$

The differentiation of this equation with respect to pressure yields an expression which reduces to

$$\frac{\partial \phi}{\partial P} = -V\beta + n_1V_1\beta_1 = \left(\frac{\partial k}{\partial P} + \frac{k}{2}\beta\right)c^{\frac{1}{2}} - \bar{B}^0$$

Now, substituting $(V - \phi)$ for n_1V_1, $\frac{1000}{c}$ for V, and $kc^{\frac{1}{2}} + \phi^0$ for ϕ, we get:

$$\left(\frac{1000}{c} + \frac{k}{2}c^{\frac{1}{2}}\right)\beta = -\frac{\partial k}{\partial P}c^{\frac{1}{2}} + \left[\frac{1000}{c} - (kc^{\frac{1}{2}} + \phi^0)\right]\beta_1 + \bar{B}^0$$

which finally takes the form

$$\beta = \frac{1}{1 + \frac{k}{2000}c^{\frac{3}{2}}}\left[\beta_1 + Ac - Dc^{\frac{3}{2}}\right] \qquad (6)$$

where the constant A is

$$\left(\frac{\bar{B}^0 - \beta_1\phi}{1000}\right)$$

and D is

$$\left(\frac{\frac{\partial k}{\partial P} + k\beta_1}{1000}\right)$$

Attention should be called to the fact that this expression for β as a function of concentration depends only on Masson's equation. Since it includes all the constants which we have obtained from the plots shown in figures 1 and 2, a good check on the consistency of our operations would be afforded by a comparison of the calculated and observed values of β. The necessary calculations have been carried out and the average absolute differences between calculated and observed β values are listed below:

Salt	NaCl	NaBr	NaI	KCl	KBr	KI
Number of solutions	5	4	4	3	4	5
Average difference	0.07	0.03	0.05	0.07	0.06	0.06

The magnitude of these differences is only slightly greater than the estimated uncertainties of the compressibility measurements. It should be noted, however, that in practically all cases the calculated β values were smaller than the observed ones. This difficulty arises from the fact that β is not the ideal coefficient and that the calculation of c_{200} is an approximation. To illustrate the sensitiveness of equation 6 to the last-named factor, it may be mentioned that an average increase of 0.05 unit in $\frac{\partial k}{\partial P}$ would completely remove the apparent defect in the calculated β values.

From the combination of his $\bar{B} - c^{\frac{1}{2}}$ and Masson's equation, Gucker (10) derived an expression which is the same as equation 6 with the denominator term missing. His derivation may be questioned on the ground that his apparent compressibility function is not mathematically consistent with Masson's equation.

The consideration of the significance of the apparent volume and the apparent compressibility is most conveniently approached from the standpoint of the relationship that exists between them. This relationship is gotten directly by eliminating the $c^{\frac{1}{2}}$ term from equations 3 and 5 and is

$$(\bar{B} + f)_c = \left(\frac{\partial \ln k}{\partial P}\right)\phi_c + \text{const.}$$

The subscript c is used to indicate that the two variables refer to the same

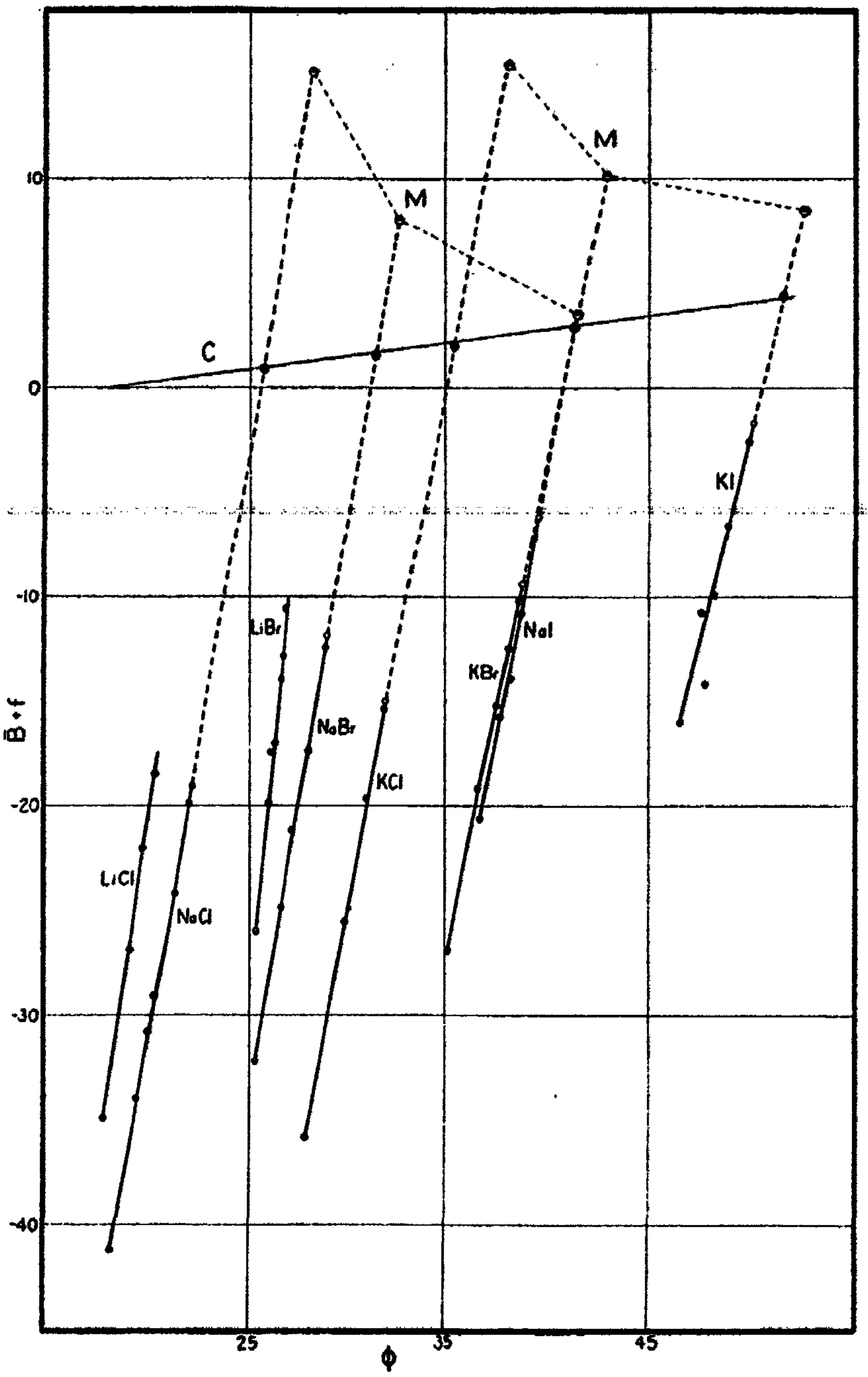

Fig. 3. Plot Showing the Linear Relationship between the Apparent Compressibility Factor ($\bar{B} + f$) and the Apparent Volume of the Solute as the Solution Concentration Changes

concentration. Values of the coefficient $\frac{\partial \ln k}{\partial P}$ have already been given in table 3. The "constant" is equal to $(\bar{B}^0 - \frac{\partial \ln k}{\partial P} \phi^0)$. In figure 3 this linear relationship is depicted for the eight solutions for which we have the necessary data (table 1). In the direction of decreasing $\bar{B}$ and ϕ the lines have been extended only to the point where the values of the two variables correspond to those derived from figures 1 and 2 for infinitely dilute solution, $c = 0$. The other extreme of the actual solution state, the saturated solution, is indicated on each line by an open circle.

In taking up the examination of this graph we shall consider first an interpretation of the plotted terms. The apparent volume is usually regarded as equal to the volume of the solute (ϕ^*) minus the contraction (κ) undergone by the solvent:

$$\phi = \phi^* - \kappa \tag{7}$$

The mechanism of the contraction is not clearly established. By some investigators it is represented as a compression of the solvent (electrostriction theory), and by others as a change in the grouping of the water molecules (polymerization theory and structural theory). Since the volume of the solute is supposed to be practically constant, the change in ϕ with concentration would have to be attributed to a change in κ. From the viewpoint of even this simplified picture of ϕ, the $\bar{B}$ concept is relatively complex. The magnitude of the calculated quantity $\bar{B}\left[= -\frac{\partial \phi}{\partial P}\right]$ may be looked upon as the net result of three different effects produced by pressure: (1) a decrease in the contraction $\left(-\frac{\partial \kappa}{\partial P}\right)$ which would act to increase ϕ and which probably overshadows the other effects; (2) a decrease in the domain of the solute $\left(-\frac{\partial \phi^*}{\partial P}\right)$ which would tend to decrease ϕ; and (3) an increase in the concentration which normally produces an increase in ϕ. The increase in ϕ which results from this increase in concentration is, as has already been pointed out, equal to the factor f. Hence the plotted term $(\bar{B} + f)$ represents only the resultant of the two effects described above under (1) and (2).

With regard to these two opposing effects some further qualitative comments may be made. The magnitude of the contraction κ is conceivably determined by the properties of the individual ions, by the amount of the solvent affected, and by the state of the solvent. If pressure altered only the last factor (e.g., decrease in polymerization), it is conceivable that the resulting change $\left(-\frac{\partial \kappa}{\partial P}\right)$ would be proportional to the initial value of the contraction. The magnitude of the variation in the domain of the solute $\left(-\frac{\partial\phi^*}{\partial P}\right)$ would depend primarily on the nature of the environment (oppositely charged ions or solvent molecules) and would therefore vary with concentration. It may be remarked here also that positively and negatively charged ions might differ considerably in their action on the water. Such a difference would be reflected in the magnitude of the quantities κ, $\frac{\partial\kappa}{\partial P}$, and $\frac{\partial\phi^*}{\partial P}$.

On the basis of the foregoing interpretation of the plotted terms it will be of interest to consider certain features of the graph. We may look upon the infinitely dilute solution as the simplest state because of the absence of the complicating interionic effects, but even here a definite analysis of the "apparent" concepts faces obvious difficulties. Thus, although the contraction presumably has a maximum value, its magnitude is unknown. Similarly, the significance of the various $\bar{B}^0$ values is obscure because the value of neither component factor is known. Attention should perhaps be called to the fact that both the ϕ^0 and $\bar{B}^0$ values of the solutions of the two lithium salts are abnormally high, if the solutions of the sodium and potassium salts can be regarded as normal. This irregularity is undoubtedly associated with the assumed existence of chemically hydrated lithium ions. In this case if the limited amount of water of hydration has undergone a large contraction, it must be supposed that the hydrated ion has less effect on the solvent than the simple unhydrated ion would have.

The existence of a linear relation between $\bar{B} + f$ and ϕ is somewhat puzzling because it means that the changes in κ and the net change in $\left(-\frac{\partial\kappa}{\partial P} + \left(-\frac{\partial\phi^*}{\partial P}\right)\right)$ resulting from a change in concentration are proportional over the entire concentration range of solution. This statement of the relationship would be quite understandable if the $\frac{\partial\phi^*}{\partial P}$ term were independent of concentration because of the possible direct dependence of $\frac{\partial\kappa}{\partial P}$ on the magnitude of κ. To take account of the presence of the $\frac{\partial\phi^*}{\partial P}$ term it would be *necessary to assume that the variation in this term also is directly* proportional to κ. A possible mechanism can be pictured as follows. It may be supposed that only the solvent molecules in direct contact with an ion are involved in the contraction of the solvent. It may be imagined further that with increasing concentration of the solution, these molecules are partially replaced by oppositely charged ions, resulting in a decrease in κ and a variation in the magnitude of $\frac{\partial\phi^*}{\partial P}$. If these two effects were proportional to the number of solvent molecules displaced, then the $\frac{\partial \phi^*}{\partial P}$ factor might, like $\frac{\partial \kappa}{\partial P}$, be proportional to κ. In short, this argument would lead to the conclusion that the slopes $\frac{\partial \ln k}{\partial P}$ of the lines drawn in figure 3 are the sum of two proportionality factors, one representing the relationship between κ and $\frac{\partial \kappa}{\partial P}$, which would be the same for all solutions, and the other, the relationship between κ and $\frac{\partial \phi^*}{\partial P}$, which would depend on the difference between the ion–ion and the ion–solvent forces. The fact that the slopes of the lines are very nearly the same would seem to be in accord with this simplified argument. An attempt to find a quantitative expression for $\frac{\partial \ln k}{\partial P}$ in accord with the foregoing interpretation, resulted in the following:

TABLE 5

Data bearing on the C-state

SALT	$\beta_{\text{salt}} \times 10^6$	ϕ_c^*	V_c
NaCl	4.26	25.7	50.4
NaBr	5.07	31.5	46.6
NaI	7.08	41.5	44.2
KCl	5.63	35.5	70.1
KBr	6.70	41.5	68.2
KI	8.54	51.6	76.7

$$-\frac{\partial \ln k}{\partial P} = 7.48 \times 10^{-4} - (\beta_{\text{salt}} \cdot \beta_1)10^6 \qquad (8)$$

Values of the slopes calculated by means of this equation, using the β_{salt} data given in table 5, are given in the last column of table 3. They are in good agreement with the values derived from the experimental data. Although the expression is of the type expected, it is nevertheless only empirical. It is a curious fact that the figure 7.48 × 10^{-4} is exactly the molal compressibility of pure water.

Up to this point in our discussion we have attempted to sketch an interpretation of the apparent molal compressibility concept along rather conventional lines. In this case, as with other relationships involving the "apparent" properties of solutes, a more definite treatment is out of the question until at least one of the unknown component factors can be established with some degree of certainty. It may be of interest therefore to describe briefly a possible procedure for estimating the volume of the solute ϕ^* on the basis of the relationships we have been considering.

The problem resolves itself into an estimation of $\phi = \phi^*$ in the hypothetical limiting solution state where the number of moles of water present is zero, because in this state κ would be presumably zero. The procedure which we shall employ rests on two postulates which may be stated here: (1) the variation of ϕ and $(\bar{B} + f)$ with concentration beyond the saturated state[3] is the same as obtained in actual solution and can be represented by equations 3 and 5, respectively; and (2) the volume of the solute is independent of concentration.

Masson sought to calculate the desired limiting value ϕ^* directly. If the condition $n = 0$ is imposed (equation 1), the resulting maximum value of the apparent molal volume ϕ_m can be calculated readily with the aid of the Masson constants. *The acceptance of the ϕ_m state as the desired hypothetical* limiting state has been questioned (17) on the ground that the condition employed ($n = 0$) does not take into account the forces (interionic and ionic–solvent) which are effective in the solution state.

The condition which we propose to use for the estimation of the hypothetical critical state is the compressibility of the crystalline solute. The basis for this condition is to be found in the fact that a part of the ions in concentrated solutions must be in contact. It is reasonable to suppose, therefore, that these ions in contact are subject to the same mutual forces as in the crystalline state and that they tend to form aggregates of a crystalline character. Since the fraction of ions in contact increases with concentration, it may be imagined that the desired limiting state corresponds to the concentration where all the ions form part of lattice fragments. Such a supposition is not in conflict with the present theories of concentrated solutions. Its plausibility is also suggested by some of the properties of the Masson relationship. Thus, the constant k appears (16) to be a function of the crystal ionic radii. Further, it has been shown (17) that the ϕ_m values of the alkali halides are linearly related to the corresponding volumes of the crystalline salts. In this connection, too, it is perhaps significant that the compressibility of the crystalline salt can be used in equation 8.

The concentration at which the solute has the same compressibility as in the crystalline form is readily calculated. Since $(\bar{B} + f)$ is the molal compressibility of the solute and ϕ_c^* in the limiting state would be the molal

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[3] Longworth (J. Am. Chem. Soc. 54, 2748 (1932)) gives another empirical relationship between ϕ and the number of moles of water in sodium chloride solutions, which, he points out, gives directly a value of $\phi^* = (=22.85)$.

volume of the solute, it is only necessary to solve equations 3 and 5 for the concentration which satisfies the condition:

$$\frac{\bar{B}+f}{\phi_c^*} = \beta_{salt}$$

These critical concentrations of the solutions of the sodium and potassium salts have been determined in this way, using the data already given in this paper. The β_{salt} values used were from the measurements of Bridgman (3) and were recalculated to express the volume change per metric atmosphere instead of kilogram per square centimeter. The volume of the solute ϕ_c^* and the volume of the solution V_c corresponding to this concentration have also been calculated and are presented in the following table. To avoid confusion we shall designate these properties with the subscript c and shall refer to the solution at this particular concentration as the C-state. It may be remarked here that from the nature of the calculations the ϕ_c^* values have only a slight uncertainty, whereas the V_c values are in error possibly by several per cent.

Points representing these values of $(\bar{B} + f)_c$ and ϕ_c^* are plotted in figure 3. The relation between these two quantities appears to be represented quite satisfactorily by the straight line C. It is a rather curious fact that this line shows $(\bar{B} + f)_c$ to become zero when ϕ_c^* equals 18 cc., the volume of 1 mole of water. The importance of the C-state to our problem is that it furnishes us with an estimate of the minimum value of the solute volume ϕ^*. Regardless of the actual volume of the solute, its compressibility could hardly be less than that of the crystalline solid, in which state the ions are packed most closely and the repulsive forces between them are greatest. The maximum value of the solute volume would, as we have already indicated, be ϕ_m and, for the sake of comparison, these values are also plotted in figure 3. Two lines, M, are drawn through points representing salts with a common cation.

In the case of the iodides there is very little difference between the C- and M-states, a fact which enables the solute volume to be established within narrow limits. With regard to the chlorides and bromides the situation is not so simple. In the case of the bromides, however, there is one cogent argument against the acceptance of the M-state as the limiting solution state. The ϕ_m values of these salts are slightly less than the volumes of the crystalline salts, and yet the compressibility of the former is four or five times greater than the latter. Another fact in favor of the acceptance of the ϕ_c^* values as close approximations of the volume of the solute in solution is the close agreement with values found in an entirely different way. It has been shown (19) that the apparent molal volume of a salt in saturated solutions at different temperatures varies linearly with the square of the number of moles of water present in the solution. This relationship yields a value of the solute volume ϕ_s^* for the solution state where the number of moles of water present is explicitly zero. The ratios between ϕ_s^* and ϕ_c^* are as follows:

Salt	NaCl	NaBr	NaI	KCl	KBr	KI
ϕ_s^*/ϕ_c^*	—	1.00	1.03	0.97	1.00	1.06

Some difference between the two sets of volumes would be expected because the ϕ_s^* values correspond to solutions at different and unknown high temperatures. The effect of temperature would not be expected to be very great, and therefore the fact that the ratios given above are not far from unity is further evidence in support of our interpretation of the ϕ_c^* values.

An objection to our determination of the *C*-state might be found in the manner in which the compressibility coefficient of the solution varies with concentration in this hypothetical region of the solution state. According to equation 6 the coefficient of each solution passes through a minimum. Since this fact may be of importance to our argument, the necessary data are tabulated in table 6. A comparison of the concentrations corresponding to the *C*-state and the minimum in the compressibility coefficient shows that for three of the salts the *C*-state is in a region where β is increasing with concentration. If this condition is physically unreal, then the extrapolation of Masson's and the derived relationships to the *C*-state would be of questionable legitimacy. On the other hand, the choice of $\beta_{\text{min.}}$ for the limit of the solution state yields negative values of $\bar{B} + f$ which are also absurd physically. It is difficult to decide how much significance is to be assigned to a minimum in the compressibility coefficient of a binary mixture, because a change in concentration produces a change in the amounts of both solute and solvent in a unit of volume. Perhaps a less obscure factor would be the compressibility of a volume of a solution con-

TABLE 6

Data for the comparison of the C-state and $\beta_{\text{min.}}$

SALT	CONCENTRATION OF *C*-STATE	CONCENTRATION OF $\beta_{\text{min.}}$	β AT *C*-STATE	β AT $\beta_{\text{min.}}$	VALUES OF f AT *C*-STATE
NaCl	19.6	14.0	21.0	18.9	0.82
NaBr	21.5	18.5	15.9	15.4	0.50
NaI	22.6	25.0	11.7	11.0	0.22
KCl	14.3	13.0	22.3	22.0	0.84
KBr	14.7	16.0	19.2	19.1	0.52
KI	13.0	23.0	18.8	15.0	0.47

taining 1 mole of solute (βV), because the variation which it undergoes with a change in concentration could be ascribed primarily to the loss of solvent. For the solutions under consideration, this property, the molecular solution compressibility, passes through a minimum at concentrations greater than those of the C-state. As a matter of fact, in the case of the sodium salts the concentrations of these minima and those of the C-state are almost the same. With regard to the factor f, which is a function of both the compressibility and the concentration, the following brief account may be given. As can be seen from the data in table 1, f with increasing concentration increases rapidly at first and then tends to approach a constant value. In the hypothetical region of the solution f begins to increase again quite sharply, the point of inflection occuring very nearly at the same concentration as the minimum in β. Values of f at the C-state are included in table 6, and, with the exception of the figures for the chlorides, they are not very much larger than the values of f in the saturated solution. For the sake of completeness this table includes values of the minimum value of β and also the β value at the C-state, as calculated by equation 6.

Because of the doubt which the compressibility minima cast on the significance of the $\phi_c{}^*$ values, especially in the case of the chlorides, additional evidence in support of the calculated solute volume of sodium chloride is quite welcome. From the standpoint of our interpretation of the apparent volume as expressed by equation 7, the solute volume becomes equal to the apparent volume when the contraction κ becomes zero. Our procedure for the calculation of $\phi_c{}^*$ was based on the assumption that when no solvent is present in the solution, κ must equal zero. There is another way in which κ can be made negligibly small or zero. In accordance with the polymerization or structural theories of water we may postulate that the contraction results only from a change of the complex molecular state to a simple molecular state. Increase in pressure is supposed to reduce the number of complex molecules and thereby to act to diminish the magnitude of the possible contraction. It is this process which we have supposed to be the cause of the increase in the apparent volume with pressure. By increasing the pressure on a solution system sufficiently, the fraction of the complex molecules present should approach zero, and the apparent volume should accordingly approach a constant limiting value which we would identify as the solute volume. Data with which to test this argument are to be found in the extensive series of measurements made by Adams with sodium chloride solutions at 25°C. The apparent molal volume at infinite dilution varies with pressure as follows:

Pressure in atmospheres	1	2000	5000	7000	8000	9000	10,000
ϕ^0 in cc	17.0	21.9	24.4	25.2	25.3	25.4	25.5

These volumes show the expected variation with pressure. From the graph (figure 8) given by Adams (1) the limiting value would appear to be slightly less than 25.7 cc., which is the value of ϕ_c^* calculated for sodium chloride. The agreement between the two entirely different estimations of the solute volume can be looked upon as support of our interpretation of the ϕ_c^* values. In this connection it is noteworthy that the volume of the crystalline salt at high pressures is not very different from the solute volume. According to Adams' graph the volume of the salt becomes 25.8 cc. under a pressure of 1.2×10^3 atmospheres instead of 27.0 cc. at atmospheric pressure. At this high pressure there remains practically no free space in the crystal lattice, and the volume of the salt must be very nearly that of the domains of the constituent ions.

In view of the possibility that the calculated ϕ_c^* values might represent the volume of the solute in solution, it will be of interest to consider briefly some of the conclusions to which they lead. In the first place it should be noted that the ϕ_c^* values are additive; thus, the differences between the three anions are:

M	MBr − MCl	MI − MBr
	cc.	cc.
Na	5.8	10.0
K	6.0	10.1
Calculated	5.6	9.9

This particular set of differences is given because it affords a clue to the meaning of the term "volume of solute.". If we assume that the anions have the same radii as in the crystal lattice, then the differences found are practically the differences in volumes of cubo-octahedra circumscribed about the ionic spheres. These calculated differences are given in the last row of the above tabulation. This outcome is in accord with the supposition (17) that the volume of the solute in solution is the domain of exclusion, the space within which adjacent ions or water molecules do not penetrate. If for the purpose of calculation we assume that the anion volumes are the volumes of these cubo-octahedra, then the volumes of the cations in the different salts are as follows:

	Chloride	*Bromide*	*Iodide*	*Cube*	*Cubo-octahedron*
Na	3.6	3.8	3.9	4.2	3.2
K	13.4	13.8	14.0	11.4	8.8

Two different calculated volumes of the crystal ions are also given to show that the order of magnitude of the cation volumes in solution is what might be expected if they are the domains of exclusion of the crystal ions.

The domain of exclusion of an ion probably depends somewhat on whether the ion is surrounded by oppositely charged ions (*C*-state) or water molecules (infinite dilution). If we assume, however, that the change is negligibly small, then according to equation 7, the difference $\phi_c^* - \phi^0$ is equal to the maximum contraction which the water undergoes as a result of the ionic forces. Values of this contraction are given below:

Salt	NaCl	NaBr	NaI	KCl	KBr	KI
$(\phi_c^* - \phi^0)$ in cc	7.5	6.2	4.6	7.6	6.3	5.1

A scrutiny of these figures reveals at once that κ depends only on the anion involved. This could mean that sodium and potassium ions produce no contraction or that they produce the same contraction. No decision between these alternatives can be made at this time. That there is a decided difference between the influence of the cation and anion and that the influence of the latter is predominant has been conjectured by several investigators on other grounds.

Using these figures for the contraction of the solvent, it is possible to carry out a number of interesting calculations. For instance, fairly good estimates can be made of the number of water molecules affected and also of the compressibility of the solute domain in infinite dilution. These suggested calculations have been made and yield quite plausible results. There is no point in considering them, however, until the interpretation of the basic ϕ_c^* values is better established.

In concluding this study a brief reference will be made to earlier work dealing with the compressibility of solutions. Röntgen and Schneider (14) proposed a simple formula for the variation of β with percentage concentration of salt in solution. For a time they believed that at the upper limit of the solution state (per cent salt = 100), β became equal to β_{salt}. This view is of interest because our calculation of the *C*-state makes use of the same assumption in a somewhat different form.

In 1897 Gilbault (8) published the results of an extensive series of compressibility measurements of salt solutions at 20°C. over the pressure range 0 to 300 atmospheres. He concluded that the variation of the compressibility could be represented by an expression which may be written as follows:

$$\frac{(\ln \mu_0 - \ln \mu)d}{a \cdot d_1} = k$$

where μ_0 = the compression of 1 mole of water $\dfrac{18}{d_1}\beta_1$

μ = the "molecular compressibility" of the solution. If we let ν = number of ions per molecule of salt, N = moles of water per mole of salt, and c = concentration in moles per liter, then

$$\mu = \frac{1000}{c(N + \nu)} \cdot \beta$$

$$a = \frac{\nu}{N + \nu}$$

d, d_1 = densities of solution and pure water, respectively.

k = a constant characteristic of each salt.

The significance of this equation lies in the utilization of μ, which gives the volume change of an amount of solution that contains always the same total number of water molecules and ions.

Gilbault calculated the values of k for eighteen salt solutions and found them to be constant within 0.3 per cent over a wide concentration range. Permann and Urry (12) recently tested the equation with their compressibility data for solutions of sucrose, urea, potassium chloride, and calcium chloride over the temperature range 30–80°C. and found that the agreement between the calculated and observed values of β "is surprisingly good considering the range of concentration covered. It suggests that dissociation is complete in electrolytic solution, thus confirming the theory of Debye and Hückel." On the other hand, a test of Gilbault's equation with our data reveals the equation to be quite unsatisfactory. For example, as can be seen in table 7, the calculated values of the characteristic constant vary markedly with concentration. Curiously enough, practically constant values of $k = 1.562$ are obtained for the chloride solutions if the compressibility of water is taken equal to 42.4×10^{-6} instead of 41.8×10^{-6}. But in order to get fairly constant k values for the bromide solutions a still higher value for β_1 (43.6×10^{-6}) must be assumed. This result would indicate that the original equation is insufficient to represent the variation of β with composition and density of the solution and that the equation requires another factor, constant for each solute, added to the

TABLE 7

Variation of calculated values of k with concentration

SALT	CONCENTRATION	k (CALCULATED)	SALT	CONCENTRATION	k (CALCULATED)
NaCl	5.008	1.518	NaBr	7.396	1.667
	3.246	1.492		4.099	1.461
	1.657	1.446		2.307	1.268
	1.087	1.401		1.206	1.237
	0.497	1.329			

term. The only other criticism to which Gilbault's equation has been subjected was made by Tamman (21), who pointed out that the experimental precision claimed by Gilbault would mean that the temperature of his thermostat bath was held constant to within 0.0001°C. Tamman estimates that the actual uncertainty in Gilbault's data amounts to 1 to 3 per cent and in some cases may be even greater.

The reason for considering Gilbault's equation in such detail is the relationship between the "constant" k and our factor $\bar{B}^0$. Taking μ_0 equal to $V_1\beta_1$ and μ equal to $(1 - a)\, V_1\beta_1 - \frac{a\bar{B}^0}{\nu}$, we can write Gilbault's expression as

$$\bar{B} = V_1\beta_1\nu\left(\frac{1 - e^{-ka\frac{d_1}{d}}}{a} - 1\right)$$

Since at infinite dilution a approaches 0, we have

$$\bar{B}^0 = V_1\beta_1\nu\,(k - 1)$$

In other words, for a series of salts of the same valence type $\bar{B}^0$ should be linearly related to the Gilbault constant k. The values of $\bar{B}^0$ calculated from the k values given by Gilbault cannot be compared with our $\bar{B}^0$ values because of the difference in temperature involved. However, the difference between the two sets of $\bar{B}^0$ values is not only too large to be attributed solely to the effect of temperature but depends in magnitude on the cation of the salt. If we use the information obtained from our data for sodium chloride solutions ($k = 1.562$ when $\beta_1 = 42.4 \times 10^{-6}$), $\bar{B}^0$, calculated by the above equation, is 39.8×10^{-4}. This figure is not exactly the same as that (41.2×10^{-4}) given in table 1 but the difference may arise from the fact that the last figure applies to systems under 200 atmospheres, whereas the other has not been calculated so rigorously. In any case it may be concluded that Gilbault's equation in the original form is too simple and that the introduction of another factor as was suggested above may perhaps remedy the difficulty.

SUMMARY

Evidence is presented to show that Masson's equation $\phi = kc^{\frac{1}{2}} + \phi^0$ is applicable to solution systems under pressures of 200 metric atmospheres.

The relationship between the apparent molal compressibility and the concentration is derived from Masson's equation. This relationship is used to determine the apparent molal compressibilities of solute at infinite dilution $\frac{\partial\phi^0}{\partial P}$, which are shown to be additive, and also the values of $\frac{\partial k}{\partial P}$ for different solutions.

By combining the apparent compressibility relationship with Masson's equation an expression is obtained which gives the compressibility coefficient of the solution (β) as a function of concentration.

The significance of the variation of the apparent compressibility with the apparent volume is considered from the standpoint of the contraction of the solvent resulting from the effect of the solute. On the basis of these considerations the volume of the solute in solution is calculated on the assumption that the limit of the solution state is reached when the compressibility coefficient of the solute in solution equals that of the crystalline salt. Although these hypothetical calculated volumes are subject to some qualification, they are shown to be of the expected order of magnitude and to be additive. The use of these solute volumes leads to the conclusion that the cations (Na^+, K^+) produce the same or no contraction of solvent, and the anions cause a contraction which decreases in the sequence Cl^-, Br^-, I^-.

The single constant of Gilbault's equation, which relates the compressibility coefficient of a solution to the density and percentage composition, is shown to be a simple function of $\frac{\partial \phi^0}{\partial P}$ and the valence type of the electrolyte. However, a test of Gilbault's equation indicates that it is not valid in the original form and that the introduction of a second constant is perhaps necessary.

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THE VISCOSITY AND FLUIDITY OF LITHIUM CHLORIDE IN ACETONE SOLUTION

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Received February 9, 1934

The viscosity of aqueous electrolyte solutions is occupying considerable attention at the present time. The empirical equation put forward by Jones and Dole (9) relating the relative fluidity, $\varphi_r = \varphi_c/\varphi_0$, to the square root of the concentration, c (in moles per liter),

$$\varphi_r = 1 - A\sqrt{c} + B \cdot c + \ldots$$

has been theoretically derived from considerations of the Debye-Hückel theory (3, 4, 5, 14), and the Falkenhagen constant "A" for a dozen electrolytes has been evaluated experimentally through numerous recent measurements (7, 8, 10, 11, 15) and the interpretation of some earlier viscosity data (1, 6, 13).

In the course of some investigations in progress in this laboratory, we found occasion to measure the viscosities of solutions of lithium chloride in acetone with sufficient accuracy to warrant interpretation of our results in the light of the interionic attraction theory as a test of the Falkenhagen equation when applied to non-aqueous solution.

EXPERIMENTAL

Apparatus

The viscometer has been previously described (7). The probable error of a determination of relative viscosity as the average of a pair of observations (from four determinations of the viscosity of acetone involving twelve observations) is, by the method of least squares, 0.02 per cent.

Materials

The lithium chloride used was "Baker's Analyzed;" it was recrystallized from conductivity water, dried, crystallized from purified acetone, and dried. The acetone used was "Coleman and Bell's C. P.;" it was distilled from alkaline permanganate, dried over anhydrous calcium chloride, and slowly redistilled. Its boiling point was 55.05°C. at 735.4 mm. (uncorrected).

Solutions

Solutions were made up by weight, the dilute solutions being made by weighing in additional acetone to a weighed portion of a more concentrated solution. The solutions were kept in closely stoppered Pyrex flasks in a dark closet; the viscosity of the most concentrated solution measured at the end of the experiments agreed with the viscosity measured at the beginning within the limit of experimental error. Concentrations were calculated to moles per kilogram of solvent, m.

Densities

The densities of acetone at 18 and 25°C. were determined as 0.7923 and 0.7844. The densities of three solutions were determined at 25°C. as follows:

m	ρ
0.1726	0.7905
0.2591	0.7932
0.3454	0.7967

These values established the relation:

$$\rho_{25} = 0.7844 + 0.036m$$

In view of the relatively small temperature interval of 7°C., constancy of the partial molal volume of lithium chloride was assumed, whence:

$$\rho_{18} = 0.7923 + 0.036m$$

From these densities, the concentrations were calculated to moles per liter of solution, c.

Data

The experimental results are summarized in table 1.

INTERPRETATION OF RESULTS

When the values of $(\eta - 1)/c$ were plotted as ordinates against the corresponding values of c as abscissas, a pair of concave sagged curves were obtained which exhibited minima at about 0.16 mole per liter. While $(\eta - 1)/c$ is strictly the slope of the chord connecting a point on the viscosity–concentration curve with the origin, it approximates the slope of the curve at the point; thus the initial downward slope of these curves corresponds to negative curvature in the η-c curves, and the minimum to a point of inflection in the latter. These plots of the "Grüneisen function" emphasize that the negative curvature of the η–c curve is more pronounced at the higher temperature, in contrast with the behavior of electrolytes in aqueous solution (1).

When the values of $(\varphi_r - 1)/\sqrt{c}$ were plotted as ordinates against the corresponding values of $\sqrt{c}$ as abscissas, the points located a pair of *approximately* straight lines which intersected the axis of $(\varphi_r - 1)/\sqrt{c}$ between -0.02 and -0.03. The "best" straight lines through the points were established by the method of least squares as:

$$(\varphi_r - 1)/\sqrt{c} = -0.0213 - 0.423\sqrt{c} \text{ at } 18°\text{C.}$$
$$(\varphi_r - 1)/\sqrt{c} = -0.0349 - 0.382\sqrt{c} \text{ at } 25°\text{C.}$$

The deviations of the fluidities calculated by these equations from the observed fluidities were considerably greater than the probable error of the measurements—about 0.15 per cent on the average—and showed a definite trend indicative of curvature. Assuming the validity of the equation of Jones and Dole,

$$\varphi_r = 1 - A\sqrt{c} - B\cdot c$$

the value of the Falkenhagen constant is 0.028, on the average.

TABLE 1

Viscosity and fluidity of lithium chloride in acetone

NO. OF RUNS	c	ρ	$\eta_c/\eta_0 = \eta$	$(\eta - 1)/C$	$\varphi_c/\varphi_0 = \varphi_r$	$\sqrt{c}$	$(\varphi_r - 1)/\sqrt{c}$	φ_c rhes
				At 18°C.				
3	0.2739	0.8046	1.14535	0.531	0.87309	0.5234	−0.2425	268.3
3	0.1368	0.7984	1.0711	0.520	0.93362	0.3699	−0.1795	286.9
4	0.07771	0.7958	1.0435	0.560	0.95830	0.2788	−0.1496	294.5
3	0.03429	0.7939	1.0211	0.615	0.97934	0.1852	−0.1116	301.0
3	0.00863	0.7927	1.0055	0.637	0.99453	0.0929	−0.0589	305.6
4	0.00431	0.7925	1.0027	0.626	0.99731	0.0657	−0.0410	306.5
10	0	0.7923	1.0000		1.00000			307.31
				At 25°C.				
5	0.2712	0.7967	1.1402	0.517	0.87704	0.5208	−0.2361	288.15
3	0.13545	0.7905	1.0685	0.506	0.93589	0.3682	−0.1742	307.5
4	0.07694	0.7879	1.0421	0.547	0.95959	0.2774	−0.1457	315.3
3	0.03395	0.7860	1.0193	0.596	0.98106	0.18425	−0.1028	322.3
4	0.00854	0.7848	1.0052	0.609	0.99483	0.0924	−0.0559	326.85
12	0	0.7844	1.0000		1.00000			328.55

Plotting $(\varphi_r - 1)/\sqrt{c}$ against $\sqrt{c}$, and $(\eta - 1)/\sqrt{c}$ against $\sqrt{c}$ on large sheets of coördinate paper, and fitting spline curves through the points, we obtained 0.024 as the graphical value of the constant at both temperatures. E. L. Vernon has privately communicated a calculated value, 0.0237 at 25°C. (cf. reference 5).

In order to bring out the inflection of the η-c curves, a function was sought which would emphasize the curvature without introducing the objectionable feature of the Grüneisen function, i.e., that the points located by small values of c become exceedingly sensitive to experimental error and tend to scatter. Such a function was found when the divergences of the observed fluidities (in rhes) from ideality were tabulated against the corresponding concentrations (table 2). The fluidity which the solution would have if it were ideal was calculated by Bingham's equation (2):

$$\Phi = \alpha\varphi_1 + \beta\varphi_2$$

where φ_1 is the fluidity of acetone and α its volume fraction in the solution;

TABLE 2

The values for the differential function, $\Delta\Phi$

c	Φ (IDEAL)	φ_c (OBSERVED)	DIFFERENCE	DIFFERENCE − 100c
At 18°C.				
0.2739	305.6	268.3	37.3	9.91
0.1368	306.45	286.9	19.55	5.87
0.07771	306.8	294.5	12.3	4.53
0.03429	307.1	301.0	6.1	2.67
0.00863	307.25	305.6	1.65	0.79
0.00431	307.3	306.5	0.8	0.37
0	307.3	307.3	0.0	0.00
At 25°C.				
0.2712	326.5	288.15	38.35	11.23
0.13545	327.5	207.5	20.0	6.455
0.07694	328.0	315.3	12.7	5.01
0.03395	328.3	322.3	6.0	2.60
0.00854	328.5	326.85	1.65	0.80
0	328.55	328.55	0.0	0.00

the fluidity of lithium chloride (solid), φ_2, is zero. Fluidities are plotted as a function of concentration in figure 1; the straight lines show the theoretical additive fluidity relationship. The slopes of the theoretical fluidity curves are computed from the solution containing 0.3454 mole of lithium chloride per kilogram of acetone: 0.2739 and 0.2712 mole per liter of solution at 18 and 25°C., respectively. The salt has a (dry) volume of 7.09 cc., the acetone a volume of 1262.15 cc. at 18°C. and 1274.86 cc. at 25°C. The volume fractions of acetone are therefore 0.9944 and 0.9937, and the fluidities (0.9944 × 307.3 =) 305.6 and (0.9937 × 328.55 =) 326.5 rhes at the two temperatures, respectively.

When values of $\Delta\Phi = \Phi - \varphi_c - 100c$ were plotted as ordinates against corresponding values of c as abscissas, an exaggeration of the curvature of fluidity-concentration curves was effected, which clearly marked the point of inflection at 0.16 mole per liter (see figure 2).

The marked positive curvature of the φ–c curves may be interpreted as evidencing some sort of combination between solvent and solute, which we may call solvation. Another evidence for solvation was adduced by a consideration of the partial molal volume. Using the densities measured at 25°C. and the equations of density derived therefrom, the apparent molal volume was computed for lithium chloride in solutions containing 1000 g. of acetone and n_2 moles of salt, over the range of concentration $n_2 = 0$ to $n_2 = 0.5$ by means of the defining relation (12):

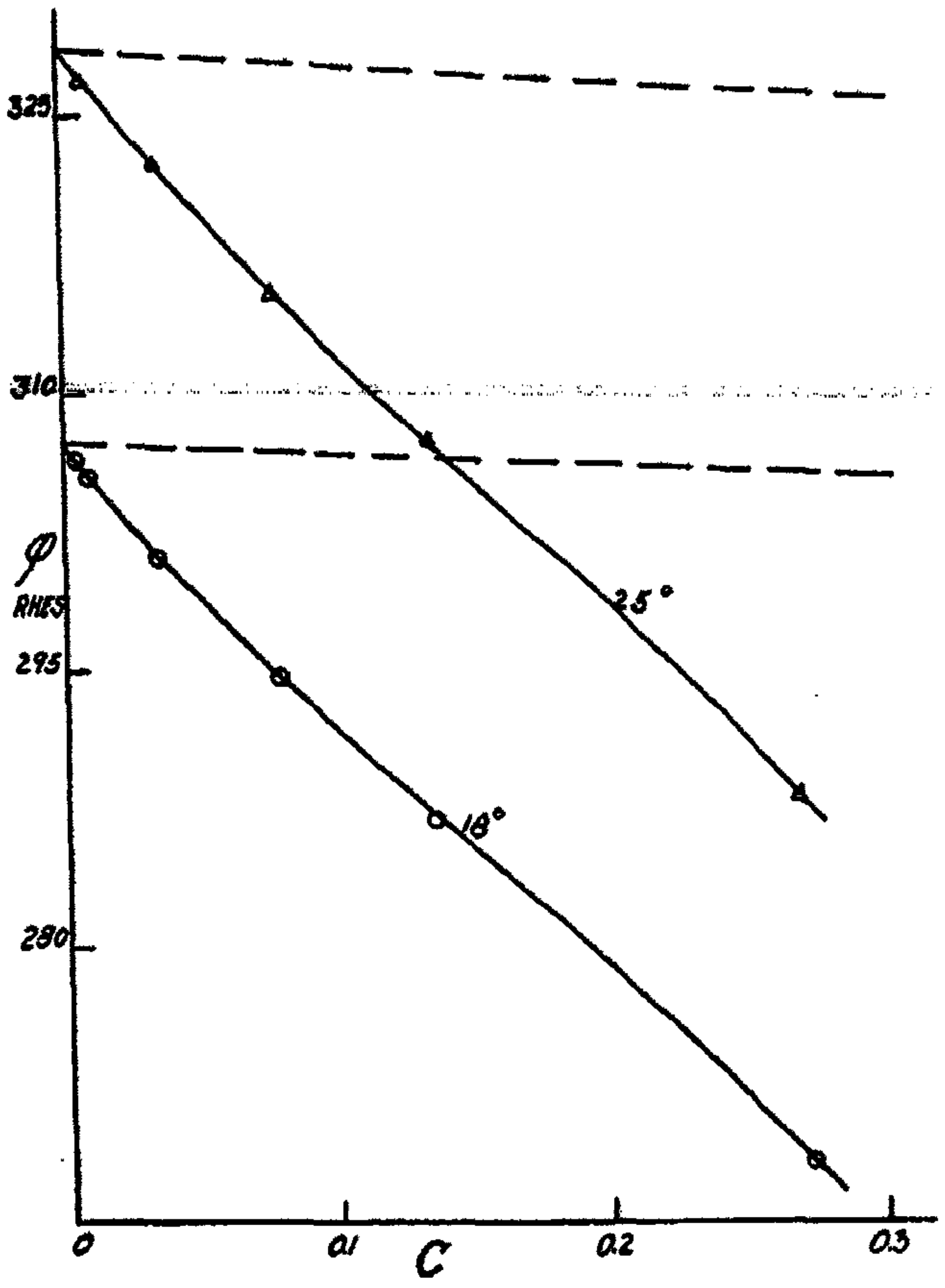

FIG. 1

$$\xi = \frac{(V - n_1 v_1)}{n_2}$$

Plots of ξ against n_2 and plots of ξ against log n_2 gave values of $\bar{v}_2$, the partial molal volume of lithium chloride, ranging from -5.0 cc. at infinite dilution to practically constant values of -4.0 cc. at 18°C. and -4.3 cc. at 25°C., over the range of concentration covered by viscosity measurements.

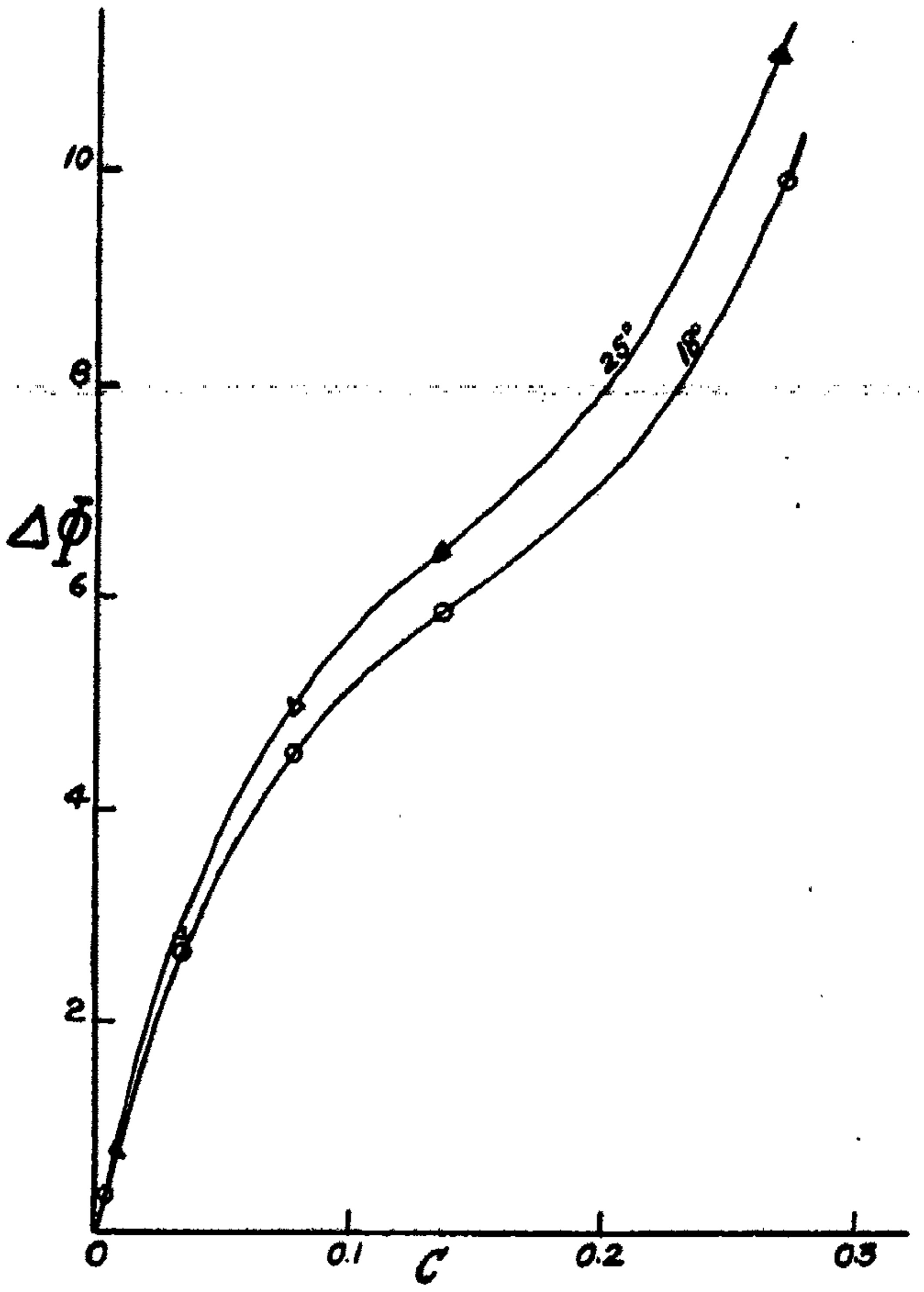

FIG. 2

The departure of the fluidity curves from ideality (figure 1), apparently measures the resultant of three factors: (1) the stiffening effect due to interionic attraction, (2) the increase in fluidity due to dissociation (1) of molecular complexes which may be supposed to exist in acetone as a pure phase, and (3) the decrease in fluidity due to solvation. By making certain assumptions, however, "apparent solvation numbers" may be calculated; consideration of these numbers appears worthy of notice.

The stiffening effect may be calculated from the Falkenhagen relation,

$$\eta = \frac{\eta_c}{\eta_0} = 1 + A\sqrt{c} + \cdots$$

which transforms into

$$\varphi_c = \varphi_0 - A\sqrt{c}\,\varphi_c - \ldots$$

where φ_0 and φ_c are the fluidities of solvent and solution (in rhes), respectively. The value of φ_c is assumed to be the fluidity of the ideal solution at the concentration c, since the Falkenhagen relation has been shown to hold in very dilute solution, and effects of dissociation and solvation are neglected. In the solution containing 0.3454 mole of lithium chloride per kilogram of solvent, there is 0.2712 mole per liter of solution at 25°C.; the observed fluidity is 288.15 rhes. This is a decrease of 38.35 rhes from the ideal fluidity, 326.5 rhes. Of this decrease, ($A\sqrt{c}\,\varphi_c =$) 4.71 rhes is due to interionic attraction. To yield a fluidity of (288.15 + 4.71 =) 292.86 rhes in ideal solution, since

$$\Phi = \alpha\varphi_1$$

it follows that the apparent volume fraction, α, is (292.86/328.55 =) 0.8914, while the ideal volume fraction is 0.9937—a decrease of 0.1023 or 10.3 per cent. The decrease in α is assumed to mean that 10.3 per cent of the acetone combines with lithium chloride to form a solvate. Since in 1000 g. of acetone there are 17.23 moles, 1.775 moles of acetone unite with 0.3454 mole of lithium chloride, an apparent solvation number of 5.14. Solvation numbers calculated similarly for the four most concentrated solutions gave as the average value 5.57 ± 0.17 at 18° C. and 5.21 ± 0.12 at 25°C., without trend. The approximate constancy of the degree of solvation is in accord with the approximate constancy of the partial molal volume.

While these numbers represent the resultant of two opposed effects, solvation tending to decrease the fluidity and dissociation of $(CH_3COCH_3)_x$ complexes tending to increase the fluidity, they approximately measure the solvation effect; for the degree of association, σ, for acetone is small in comparison with water, and the temperature coefficient of viscosity for acetone being small, it may be assumed with a high degree of probability that the increments of fluidity at 18 and 25°C. due to change in the value of σ effected by the solute are nearly equal,—for nearly equal numbers of $(CH_3COCH_3)_x$ complexes come within the sphere of influence of the solute particles at both temperatures. Thus the apparent solvation numbers are nearly proportional to the true degree of solvation.

SUMMARY AND CONCLUSION

Measurements have been made on the viscosity of acetone solutions of lithium chloride at 18°C. over the range 0.004 to 0.274 mole per liter, and at 25°C. over the range 0.008 to 0.271 mole per liter.

The stiffening effect on the solution due to the electric forces of the ions in tending to maintain a space lattice structure has been observed. The value of the constant A obtained compares favorably with the theoretical value as calculated by Falkenhagen and Vernon.

Fluidity–concentration curves are shown to be highly inflected. It is suggested that the complexity of the fluidity–concentration relationship expresses the resultant of three factors: interionic attraction—most effective at extreme dilution—and a solvation effect superimposed upon the effect which a solute itself exerts in decreasing the fluidity of the pure solvent.

Evidence for solvation is adduced, and measures of the degree of solvation are obtained.

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NEW BOOKS

Conduction of Electricity Through Gases. By SIR J. J. THOMSON AND G. P. THOMSON. Third edition, Volume II. 608 pp. Cambridge: Cambridge University Press, 1933. New York: The MacMillan Company, 1933. Price: $6.50.

The volume treating ionization by collision and gaseous discharge completes the third edition of this well-known work originated by Sir J. J. Thomson.

In spite of, or rather because of, the vast amount of material dealt with, the reviewer gets the impression that this, the third edition, cannot occupy the commanding position which the first edition did thirty years ago in the then much newer and narrower field of electrical discharge in gases. This is not meant as a criticism of the admirable compilation. The field presents so many possibilities and complexities that it has expanded enormously in various directions, experimental and theoretical. It is no longer possible to give equally adequate treatment to all the phases of the subject in the compass of two volumes. The task is not rendered easier by the fact that physics has been making major advances along a broad front with such rapidity that the conquered terrain has not yet been properly cleared up and unified in a way that makes a complete survey possible.

The volume is written in a clear readable style. The figures and tables are well presented. The first two chapters are devoted to cathode rays, the second to their wave properties, the third to electron collisions, the fourth and sixth respectively to ionization by positive ions and by x-rays, the fifth to reflected and secondary electrons from solids, the seventh to ionization by chemical reaction, the material of which is little changed from the earlier edition. Chapter VIII, of more than one hundred and fifty pages, deals with the various phenomena of gaseous discharge at low pressure. Chapters IX and X deal with the spark and the electric arc.

S. C. LIND.

The Physico-chemical Properties of Plant Saps in Relation to Phytogeography. Data on Native Vegetation in its Natural Environment. By J. ARTHUR HARRIS, late Head of the Department of Botany, University of Minnesota. Formerly Resident Botanist, Station for Experimental Evolution, the Carnegie Institution of Washington. 13.5 × 23.5 cm.; vi + 339 pp. Minneapolis: The University of Minnesota Press, 1934. Price: $4.50.

From about 1912 until his death in 1930 one of Dr. Harris' major projects was the investigation of the relationship which existed between the physicochemical properties of the leaf tissue fluids of plants and the ecological environment characteristic of the plants. He devised methods and apparatus suitable for the carrying out of physicochemical technics in field laboratories, and established his laboratories in the field where plants could be studied in their native habitats. Extensive studies were carried out on the mesophytic plants of Long Island, N. Y., the coastal plains and sand dune areas of North and South Carolina and the Island of Jamaica, the Dismal Swamp in Virginia, the Everglades and coastal swamps of Florida and Georgia, the rain forests of Jamaica and Hawaii, and the deserts, mountain slopes, arroyos, salt flats, lava fields, dunes, etc., of Arizona, Utah, California, Colorado, Washington, and Hawaii. Altogether sixteen seasons were spent in the field studies. Fragments of the data were published by Dr. Harris from time to time but the great masses of data were kept for later monographic treatment. Accordingly at the time of his death many thousands of original records remained unpublished.

A committee of his colleagues, consisting of Dr. C. O. Rosendahl, Dr. G. O. Burr, and the reviewer, were charged by President Coffman of the University of Minnesota with the task of examining the various papers of Dr. Harris and bringing to the point of publication such data as could be salvaged. The present volume is the first result of this undertaking.

After mature deliberation it was decided by the committee to publish only the "raw data" and not to attempt an analysis of the interrelationships of the various constants or to formulate an interpretation of the data in relation to the problems of phytogeography. This conclusion was reached partly because of the lack of close familiarity of the members of the committee with the plant associations which Dr. Harris had studied, and more especially because of the difficulty which the committee would face in attempting a discussion of such an enormous mass of varied data. It was felt that science might better be served by presenting the data in such form that they would be readily utilizable by other workers.

The volume opens with a reprint of a paper by Dr. Harris on "Physical Chemistry in the Service of Phytogeography" in which he discusses the types of problems toward the solution of which the data were collected. This is followed by a detailed "project outline" which he had prepared while soliciting funds for the intensive prosecution of the project, and which is accompanied by a bibliography of the forty-four papers which he had published in this field. This bibliography is followed by a contributed paper by Dr. H. L. Shantz on "The Importance of Phyto-chemical Studies in the Field of Plant Geography." This section of twenty-four pages introduces "The Experimental Data," which is essentially a single table occupying one hundred and seventy-six closely printed pages. The data are arranged alphabetically by states and within each state by the botanical names of the plants which were studied. Thus no botanical index to the volume is necessary. Physicochemical constants on more than 12,000 series of plant collections are tabulated in this section. The items recorded in the various columns are: (1) botanical name of the plant studied; (2) chemical number (a code number showing year of collection and other essential data); (3) the "station number" (a code number referring to a later "station description;" (4) the depression of the freezing point of the sap in degrees Centigrade; (5) the osmotic pressure of the sap in atmospheres calculated from Δ; (6) the specific electrical conductivity of the plant sap expressed in mhos; (7) the chloride content of the sap expressed as grams of chloride ion per liter; (8) the sulfate content of the sap similarly expressed; and (9) the pH of the sap.

Following this tabulation there are seventy-seven pages of "station descriptions," in which the geographical and botanical characteristics of the locality where the collections were made are noted. These descriptions are sufficiently exact so that another worker visiting the region should have no great difficulty in locating approximately the spot where collections were taken. These descriptions, many hundreds in total, are accompanied by a notation of the "chemical numbers" of samples taken for analysis.

The volume closes with a "chemical number" index through which those interested are enabled to find the various chemical data listed for all plants which may be growing together in any selected "station" or habitat.

The entire volume may be regarded as one enormous table of physicochemical data on plant saps. Unquestionably it contains more original data on this subject than may be found in all the rest of the literature. The data are presented without any discussion of their interrelationship. The volume should become a part of all reference libraries and all physiological libraries. Most ecologists and many physiologists will find it a mine of information.

ROSS AIKEN GORTNER.

The Chemistry of Antigens and Antibodies. By J. R. MARRACK. Medical Research Council Special Report No. 194. 16 x 25 cm. London: H. M. Stationery Office. 1934. Price: 2s. 6d. net.

During the last decade there has been an ever-growing volume of literature dealing with the basic problems of immunity in terms of the fundamental sciences. Dr. J. R. Marrack has brought together in the small space of one hundred and thirty-four pages a fairly complete collection of the most important physicochemical researches which have directly contributed to modern views concerning the nature of antigens, antibodies, and the antigen-antibody reaction.

The first chapter is devoted to certain physicochemical considerations and consists of a short and well-written survey of current views on the shapes and sizes of molecules, intermolecular forces, the structure of proteins, and the stability of suspensions. The recent evidence for and against the protein nature of antibodies is carefully reviewed in chapter II, and later in the book the specificity of artificial protein antigens, which contain "determinative" chemical groupings, is lucidly discussed in terms of structural organic chemistry.

To the chemist entering the field of immunology this monograph can be heartily recommended, for it gives a clear account of the physical and chemical studies which have served to elucidate certain immunological reactions. To the more experienced immunologist who has already realized the value of chemical concepts in the study of immunity, Dr. Marrack's book will be especially acceptable since it contains, besides a thorough survey of the recent literature, many stimulating suggestions which will doubtless form the basis of future investigations.

W. T. J. MORGAN.

A Textbook of Inorganic Chemistry. By FRITZ EPHRAIM. Second English edition by P. C. L. THORNE. 24 x 16 cm.; xii + 873 pp. London: Gurney and Jackson, 1933. Price 28/-.

In the first English edition of this work, of eight hundred and five pages, the translator made some additions to take account of English and American needs. The present edition includes much more material from the new German edition and some additions by the translator. The latter do not always go far enough. The section on Werner's theory is very valuable and satisfactory, but the reference to the new theory of the coördinate link is far too brief. The discussion of the hydrogen-palladium system leaves the subject with Hoitsema, and the newer work of Gillespie and Hall, Hanawalt, and others, is not mentioned, so that the section is quite out of date. A similar criticism could be made of the section on silicic acids, where only van Bemmelen's work appears. The phase rule diagram of silica does not include two β-tridymites; only the old methods of preparing boron hydrides are given; and in many other places the text could usefully have been brought up to date. The translation is satisfactory, although the names of Neumann and Hauck, correctly given in the German, appear as Wennann and Hanck on p. 325, Mayer instead of Mayes on p. 528, etc. The section on the thionic acids is too sketchy. The "very interesting addition compounds (nitro-metals)" of Sabatier and Senderens mentioned on p. 611, like the compounds NO_3 and H_4O_7 on p. 637, have long since passed out of existence.

The book is one which advanced students will find very useful, but it is to be regretted that the revision by the translator has not been more drastic and satisfactory. The result is, in consequence, that some parts do not give a really modern presentation of the subject.

J. R. PARTINGTON.

Chemische Technologie der Neuzeit. By OTTO DAMMER AND COLLABORATORS. Second enlarged edition in five volumes. Volume II. Part ii. 27 x 19 cm.; xvi + 888 pp. Stuttgart: Ferdinand Enke, 1933. Price: unbound, 93 M; bound, 98 M.

The present volume of this very comprehensive work deals entirely with metals: iron and steel, gold, platinum metals, aluminum, magnesium, calcium, alkali metals, beryllium, mischmetall, nickel and cobalt, silver, copper, tin, antimony, zinc, cadmium, thallium, arsenic, mercury, bismuth, lead, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, uranium, manganese, rhenium, gallium, indium, and germanium. It will be seen that the rarer metals are included, but the treatment is sometimes rather brief; for example, only four and a half pages are devoted to vanadium, and only five, one a table of analyses of ores, to tungsten. The references to literature in these sections are sometimes rather scanty. The information on the magnesium and beryllium alloys is disappointingly brief. The commoner metals are more fully dealt with, one hundred and ninety-two pages being devoted to iron and steel, seventy-two to copper, and eighty-eight to lead. The various contributors have made an attempt to deal adequately with the material in the space available and have taken good account of modern literature, including English and American, and patents. In so far as a single volume can give a satisfactory treatment of such a wide range of subjects, the present work gives a comprehensive and able survey of the field. It will need supplementing by special monographs when full information on details is required. The book is well printed and illustrated and contains many tables of numerical information, including the properties of the metals.

J. R. PARTINGTON.

Practical Methods of Biochemistry. By FREDERICK C. KOCH. Cloth; 15 x 23 cm.; viii + 280 pp.; 17 fig. Baltimore: William Wood and Company, 1934. Price: $2.25.

This is a laboratory manual in physiological chemistry, with especial reference to medical school aspects. The author has for many years been in charge of the work in physiological chemistry at the University of Chicago, and the present volume affords ample evidence that the experiments have been tried over and over again in class laboratories.

The book is divided into three parts; I, The Chemistry of Cell Constituents, including chapters on carbohydrates, lipins, proteins, nucleoproteins and nucleic acids, and hydrogen-ion concentration; II, The Chemistry of the Digestive Tract, with chapters on salivary digestion, gastric digestion, intestinal digestion and bile; and III, The Blood and Urine, with chapters on blood and hemoglobin, the quantitative analysis of blood, the quantitative analysis of urine, and the chemical examination of urine in pathological conditions. The book contains an elaborate appendix of fifty-three pages in which explicit directions are given for the preparation of the various laboratory reagents. An adequate subject index closes the volume.

In all, directions for two hundred and twenty-eight laboratory experiments are given. Most of these are for qualitative tests for various biochemical compounds. Numerous quantitative procedures are, however, included. Since the book is designed for a first course in medical biochemistry, but little use is made of physicochemical equipment or technics. This omission is the only thing that the reviewer feels calls for criticism. Since living processes are so intimately bound up with problems of osmotic pressure, permeability, electrical conductivity, and colloid behavior in general, it would seem only just that medical students should be introduced to a few simple experiments which would serve to quicken their understanding of such phenomena.

The reviewer knows of no better laboratory manual covering the field for which this text is intended.

Ross Aiken Gortner.

Many readers of This Journal will be interested in the following pamphlets published by Hermann et Cie., Paris. Each pamphlet contains a paper (including discussion) read at the 1933 Réunion internationale de chimie physique.

I. L'Effet Volta. By Emmanuel Dubois. 6 fr.
II. The Electrical Properties of Semi-conductors and Insulators. By M. A. H. Wilson. 4 fr.
III. On Phase Boundary Potentials. By Eric Keightley Rideal. 4 fr.
IV. Pile Metalliche. By O. Scarpa. 6 fr.
V. Das elektrolytische Kristallwachstum. By M. Volmer. 4 fr.
VI. Les Électrons dans les Métaux. Problèmes Statiques. Magnétisme. By F. Bloch. 5 fr.
VII. Conductibilité Électrique des Isolants et des Semi-conducteurs. By A. F. Joffé. 10 fr.
VIII. Les Électrons dans les Métaux du Point de Vue Ondulatoire. By Léon Brillouin. 9 fr.
IX. Conductibilité Électrique et Thermique des Métaux. By Léon Brillouin. 18 fr.
X. Adsorption, Electro-reduction and Overpotential at the Dropping Mercury Cathode. By J. Heyrovsky. 12 fr.
XI. Phénomènes Photoélectrochimiques. Action de la Lumière sur le Potential Métal-Solution. By René Audubert. 8 fr.
XII. Les Colloïdes et la Couche de Passage. By A. Gillet and N. Andrault de Langeron. 10 fr.
XIII. Sur le Potentiel Métal-Solution dans les Dissolvants Autres que l'Eau. By Paul Dutoit. 4 fr.
XIV. L'Effet Électro-thermique Homogène. By Carl Benedicks. 8 fr.
XV. Die Theorie der thermoelektrischen Effekte. Legierungèn, Unvollstaendige Ketten, Benedickseffekt. By Lothar Nordheim. 6 fr.
XVI. La Notion de Corpuscules et d'Atomes. By Paul Langevin. 12 fr.

F. H. MacDougall.

The Manufacture of Soda. By Te-Pang Hou. American Chemical Society Monograph No. 65. 365 pp. New York: The Chemical Catalog Co., Inc. Price: $8.00.

Dr. Hou has undoubtedly produced the first authoritative treatise on the manufacture of soda to appear in this country. The first three chapters, which are devoted to the historical development of the alkali industry, are of great interest especially to students of chemical engineering economics. They illustrate the peculiar interweaving of interests in the chemical field and the economic forces affecting the rise and downfall of a great industry. Since this is an A. C. S. monograph, it does seem unfortunate to the reviewer that more is not given of the history of the development of the Solvay process in this country and the connection with it of such great chemical pioneers as Hazard, Pennock, Trump, and Handy.

Chapter IV, on the purification of brine, is concise and well written and, perhaps, more important than the author believes, especially in this country where the quality of the brines used differs so widely. Chapter V, on the burning of limestone, is especially timely, since this important phase of the plant operation is often neglected or its importance not appreciated. The next nine chapters are devoted to a careful detailed discussion of the operations of the ammonia-soda process. The physico-chemical factors controlling the operations are given full and complete discussion. Necessarily, the description of equipment is neither quite so complete nor so modern because of the traditional policy of secrecy in which this industry has grown. Undoubtedly, it represents Dr. Hou's observations of plant practice and equipment, which can hardly be expected to cover all the newest "wrinkles" in the latter field. The reviewer is not inclined to agree with the author's statements regarding draw temperatures on p. 102 so far as general plant practice in this country is concerned.

The last twelve chapters are devoted to special alkali products, power generation, control, losses, analyses and tests, and, finally, to an all too brief chapter on plant lay-out and design. The chapter on electrolytic caustic is brief but well done, while those concerning control, losses, and analytical procedure are most excellent. The book is exceedingly well-written, clear, and forceful. Not many errors, either typographical or otherwise, were apparent to the reviewer. On p. 176 "Table 74" in the text should read "Table 79." The workmanship and materials of the book are of the usual excellent quality of this series.

This book will be of interest to students of chemical economics, industrial chemistry, and particularly the application of physical chemistry to industrial processes. To the practical chemist or engineer in the alkali industry it offers the most complete and careful account of this field which has been produced in the English language, and a careful perusal is almost sure to stimulate even the "old-timers" with a few new and useful ideas.

RALPH E. MONTONNA.

Elektrolytische Leitfähigkeit unter extremen Bedingungen. XXXVIII. Hauptversammlung der deutschen Bunsen Gesellschaft. 28 x 20 cm.: iv + 183 pp. Berlin: Verlag Chemie, 1933. Price: 8 marks.

This volume consists mainly of papers delivered at a discussion held by the Bunsen Gesellschaft on "Electrolytic Conduction under Extreme Conditions." The topics include the effect of high frequency and voltage upon electrical conductivity, electrical conductivity in non-aqueous solvents, and phenomena associated with the conduction of electricity by solids. Prominent among the contributors are Debye, Ulich, v. Hevesy, Tubandt, Lange, and Falkenhagen.

It is an interesting and important consequence of the theoretical advances in the theory of electrolytes initiated by Debye that new and profitable fields of inquiry have been opened up; this discussion indicates the advances that have already been made. As is usual with such discussions the occasion was one for stocktaking rather than for startlingly fresh announcements.

The latter half of the volume is taken up with miscellaneous papers on spectroscopy and molecular structure, electrosynthesis, and general physical chemistry.

W. F. K. WYNNE-JONES.

THE DISSOCIATION CONSTANTS OF ACETOACETIC, GLYCOLIC, AND ACETIC ACIDS IN SOLUTIONS OF SODIUM CHLORIDE

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Received February 8, 1934

In the study of the rate of bromination of acetoacetic acid in glycolate and acetate buffer solutions (7) it was necessary to know the ratio between the dissociation constants of acetoacetic acid and, respectively, glycolic and acetic acids. With the object of determining this ratio, solutions of the three acids mixed with their respective sodium salts, with or without sodium chloride, were measured with the quinhydrone electrode against a standard solution of 0.04891 *M* acetic acid + 0.05024 *M* sodium acetate. The solutions were prepared in the same way as for the kinetic experiments. As bridge solution 3.5 *M* potassium chloride was used at 25 and 18°C., while 3.0 *M* potassium chloride was used at 0°C. The buffer and bridge solution formed a sharp interface in a perpendicular, cylindrical glass tube. Unmack and Guggenheim (9) have found that this is a simple way of obtaining constant, reproducible potentials. In our calculations we have neglected the liquid-liquid potential. This error is probably of no importance when the buffer solutions mentioned above are measured against each other

Before the measurements the platinum electrodes were measured against each other in the same dilute hydrochloric acid. Only electrodes showing a potential difference of less than a few hundredths of a millivolt were used. The reliability of the electrodes during the measurement was tested in the following way. When the E.M.F. was constant (E_1), the electrodes of the two half-cells were interchanged, and the E.M.F. was again measured (E_2). The potential difference between the solutions is $E = \frac{1}{2}(E_1 + E_2)$. $|E_1 - E_2|$ was always less than 0.20 millivolt.

This method could not be used for the acetoacetate buffers. Here the potential was not constant, but decreased at a rate which was proportional to the concentration of sodium acetoacetate and independent of the concentration of acetoacetic acid. The measurements for the solution where the quickest fall was found are given in the diagram. t is the time in minutes from the addition of quinhydrone to the solution. The decrease may be explained by a reaction between the acetoacetate ion and the quinone. Owing to the linear relationship it is easy to extrapolate to $t = 0$. When the electrodes were interchanged an extra fall of the potential was noticed, as seen from the diagram. For that reason the value of E found by extrapolation of the measurements before the interchange was used. The fall was much slower at 0 than at 18°C.

The acetoacetate buffers contained a small amount of alcohol produced by the hydrolysis of the ester. Some acetate buffers to which was added a little alcohol were measured at 18°C. A decrease of $1.0 \times (C_2H_5OH) \times 10^{-3}$ volt was found. This correction was therefore added to the potentials of the acetoacetate buffers both at 18°C. and at 0°C.

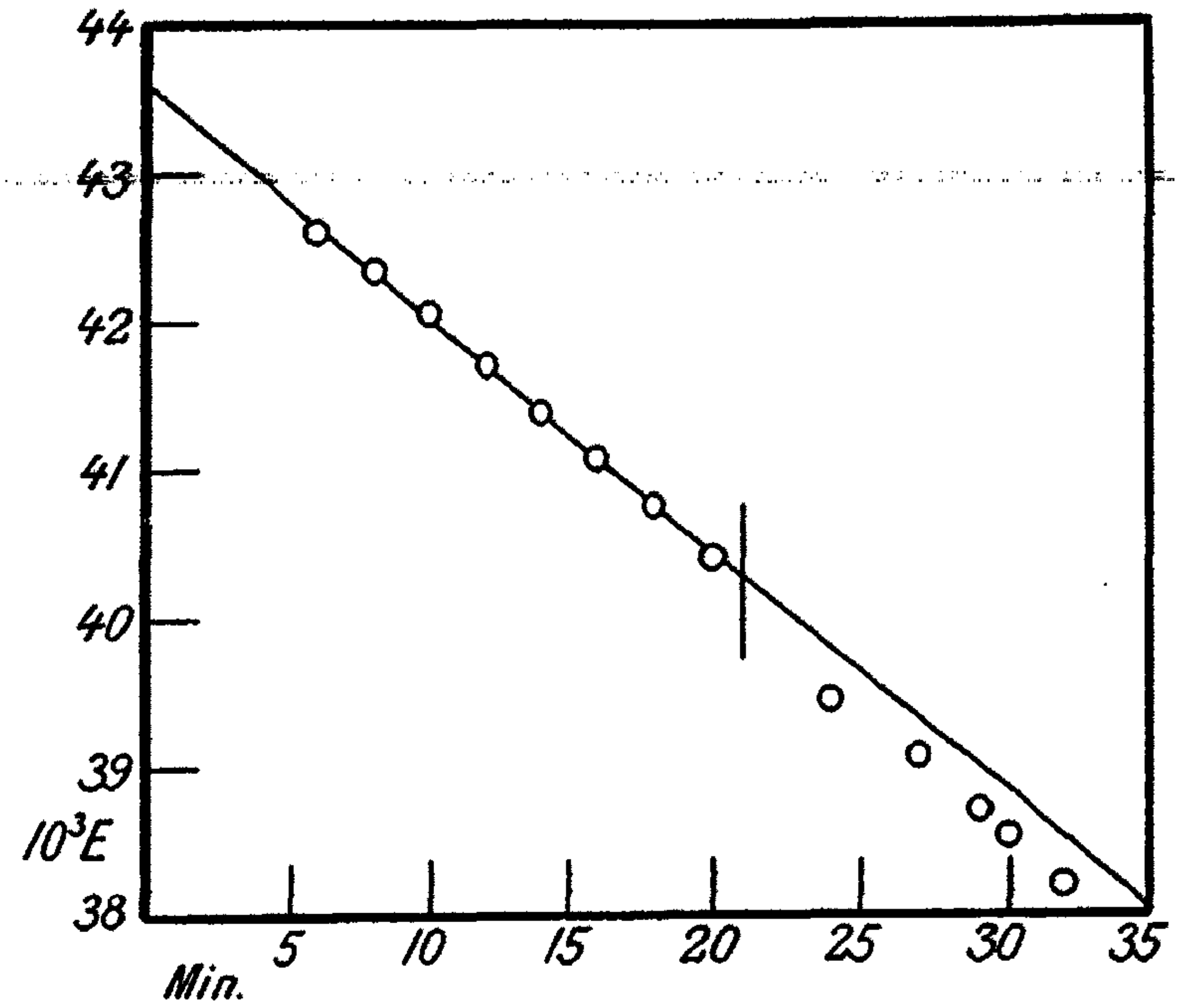

FIG. 1. THE DECREASE OF POTENTIAL IN A SOLUTION OF ACETOACETIC ACID, SODIUM ACETOACETATE, AND QUINHYDRONE

The interchange of electrodes is indicated by the crossing line.

The potential, E, of a quinhydrone electrode in a solution with the hydrogen ion activity a_{H^+}, measured against a constant standard electrode, is, when the liquid-liquid potential is neglected, given by the expression

$$\log a_{H^+} = \frac{E}{\rho} + \sigma s - C \qquad (1)$$

where

$$\rho = RT/F\log e \tag{2}$$

s is the total salt concentration, and σs the "salt error" of the quinhydrone electrode.

Between the incomplete dissociation constant K_{ac} of a weak acid HB, the dissociation constant K and the same at infinite dilution K^0, we have the following relationship,

$$K_{ac} = a_{H^+}\frac{(B^-)}{(HB)} = K^0\frac{f_{HB}}{f_{B^-}} = Kf_{H^+} \tag{3}$$

where f_{HB}, f_{B^-}, and f_{H^+} are activity coefficients of HB, B^-, and H^+, respectively.

From the equations 1 and 3 we get

$$-\log K_{ac} = C - \frac{E}{\rho} - \sigma s - \log\frac{(B^-)}{(HB)} \tag{4}$$

In a solution of univalent ions we have, according to Debye-Hückel's law,

$$-\log K_{ac} = -\log K^0 - \alpha\sqrt{s} + \beta s \tag{5}$$

α is the same for all the acids HB. β, which is dependent on the nature of the acid, approaches a constant value when $s \rightarrow 0$. Consequently the ratio between K_{ac} for the acid HB and another weak acid HB′ at the same salt concentration is determined by

$$\log\frac{K_{ac}}{K_{ac}'} = \log\frac{K^0}{K^{0\prime}} - (\beta - \beta')s \tag{6}$$

If we assume that f_{H^+} depends only on the total salt concentration, s, and not on the individual nature of B^- and B'^-, we get by means of equation 3

$$\log\frac{K}{K'} = \log\frac{K^0}{K^{0\prime}} - (\beta - \beta')s \tag{7}$$

If we use the abbreviation

$$\varphi \equiv \frac{E}{\rho} + \log\frac{(B^-)}{(HB)} - \alpha\sqrt{s} \tag{8}$$

we get from equations 4 and 5

$$\varphi = C + \log K^0 - (\beta + \sigma)s \tag{9}$$

Hence by means of equation 7

$$\log\frac{K}{K'} = \varphi - \varphi' \tag{10}$$

We calculate K/K' from the experiments by means of equation 10. For each of the solutions we find φ from expression 8. For ρ we use the values, found from equation 2, 0.05418, 0.05774, and 0.05915 at 0, 18, and 25°C., respectively. For α we use the values 0.486, 0.499, and 0.504 at 0, 18, and 25°C., respectively.

The solutions contained usually 0.05 M HB and 0.05 M NaB, to which had been added varying amounts of sodium chloride. Only a few of the solutions contained other concentrations of the acid and its sodium salt. The real concentrations of the undissociated acid HB and its ion B^- were calculated from the stoichiometric concentrations and a rough value of the hydrogen-ion concentration. The results of the measurements at 18°C. are given in table 2. The values of φ calculated from the experiments may be expressed by the formulas in table 1. The next to the ~~last column in table 2 gives δ, the difference between φ found by the meas-~~ urement and φ calculated from the formulas. It is seen that the linear relationship holds surprisingly well even at high salt concentration. At 0 and 25°C. an equally good agreement was found.

TABLE 1

Value of φ calculated from the experiments

($0.05 < s < 0.55$)

BUFFER	VALUES OF φ		
	$T = 0°C.$	$T = 18°C.$	$T = 25°C.$
Acetate	$\varphi = -0.080 - 0.336 \times s$	$\varphi = -0.086 - 0.260 \times s$	$\varphi = -0.089 - 0.240 \times s$
Glycolate	$\varphi = 0.823 - 0.118 \times s$	$\varphi = 0.833 - 0.202 \times s$	
Acetoacetate	$\varphi = 1.100 - 0.246 \times s$	$\varphi = 1.080 - 0.271 \times s$	

By means of equation 10 we now find the following expressions for the ratio L between the dissociation constants:

$$\left.\begin{array}{lll} \text{Acetoacetic acid / Glycolic acid} & 0°\text{C.} & \log L = 0.277 - 0.058 \times s \\ \text{Acetoacetic acid / Glycolic acid} & 18°\text{C.} & \log L = 0.247 - 0.069 \times s \\ \text{Acetoacetic acid / Acetic acid} & 0°\text{C.} & \log L = 1.180 + 0.000 \times s \\ \text{Acetoacetic acid / Acetic acid} & 18°\text{C.} & \log L = 1.166 - 0.005 \times s \end{array}\right\} \quad (11)$$

We have now solved our main problem. In addition we shall find the dissociation constants of the three acids, although with less accuracy than L. If we assume that the linear expressions for φ also hold when $s < 0.05$, we get directly from equation 9 the constants $C + \log K^0$ and $\beta + \sigma$. In order to determine C from equation 1 the solution 0.01009 M hydrochloric acid + 0.0898 M sodium chloride was measured against the standard buffer at 0, 18, and 25°C. According to Bjerrum and Unmack (1) the liquid-liquid potential between this solution and 3.5 M potassium chloride is so small that we may neglect it. For the activity coefficient of the

TABLE 2

Measurements with the quinhydrone electrode in buffer solutions at 18°C.

E for the acetoacetate buffers has been corrected for the effect of the alcohol

BUFFER	(HB) (STOICH.)	(NaB) (STOICH.)	(NaCl)	$E \times 10^3$	$\log\frac{(B^-)}{(HB)}$	s	φ	$\delta \times 10^3$	$-\log K$
Acetate	0.04891	0.05024	0.000	0.00	0.0122	0.050	−0.100	−1	4.598
	0.1489	0.05024	0.000	28.16	−0.4709	0.050	−0.096	+3	4.594
	0.04891	0.05024	0.050	1.86	0.0122	0.100	−0.113	0	4.557
	0.09782	0.1005	0.000	1.20	0.0118	0.100	−0.125	−12	4.568
	0.04891	0.05024	0.149	4.06	0.0122	0.199	−0.140	−1	4.513
	0.04891	0.05024	0.250	5.46	0.0122	0.300	−0.166	0	4.488
	0.04891	0.05024	0.500	7.49	0.0122	0.550	−0.228	+4	4.462
Glycolate	0.04808	0.05000	0.000	52.80	0.0206	0.050	0.822	−1	3.676
	0.1046	0.05000	0.000	72.45	−0.3183	0.050	0.824	+1	3.674
	0.04808	0.05000	0.050	54.86	0.0209	0.100	0.813	0	3.630
	0.04808	0.05000	0.050	54.88	0.0209	0.100	0.814	+1	3.630
	0.04808	0.05000	0.149	57.38	0.0216	0.199	0.793	0	3.580
	0.04808	0.05000	0.250	58.90	0.0216	0.300	0.768	−4	3.553
	0.04808	0.05000	0.500	61.53	0.0218	0.550	0.718	−4	3.516
Aceto-acetate	0.02041	0.02056	0.024	67.12	0.0182	0.045	1.076	+8	3.430
	0.0514	0.0505	0.060	70.27	−0.0008	0.111	1.050	0	3.384
	0.0511	0.0499	0.060	70.47	−0.0034	0.110	1.051	+1	3.384
	0.0511	0.0503	0.060	69.81	0.0000	0.110	1.044	−6	3.392
	0.0769	0.0251	0.085	97.36	−0.4591	0.111	1.061	+11	3.374
	0.0269	0.0749	0.036	43.72	0.4469	0.110	1.039	−11	3.396
	0.0511	0.0498	0.160	72.48	−0.0043	0.210	1.022	−1	3.344
	0.0514	0.0505	0.260	73.48	0.0008	0.311	0.996	0	3.321
	0.0510	0.0499	0.460	75.38	−0.0009	0.510	0.949	+7	3.297

TABLE 3

TEMPERATURE	ACETIC ACID			GLYCOLIC ACID			ACETOACETIC ACID		
	$-\log K^0$	β	$K^0 \times 10^5$	$-\log K^0$	β	$K^0 \times 10^4$	$-\log K^0$	β	$K^0 \times 10^4$
°C.									
0	4.770	0.287	1.70	3.867	0.139	1.36	3.590	0.197	2.57
18	4.748	0.217	1.79	3.829§	0.153	1.48	3.582¶	0.222	2.62
25	4.751†	0.191	1.77	(3.812)*		(1.54)‡			

* The data in parenthesis have been found by extrapolation from 0 and 18°C.

Other determinations:

† MacInnes and Shedlovsky (6), conductivity, 4.756.

Harned and Ehlers (3), concentration cells without liquid junction, 4.756.

‡ Böeseken and Kalshoven (2), conductivity, 1.54×10^{-4}.

§ Larsson and Adell (4), quinhydrone electrode, 3.835.

¶ Widmark (10), hydrogen electrode at about 16°C., 3.55.

Ljunggren (5), kinetic measurements at 25°C., 3.66.

hydrogen ion in sodium chloride solutions ($0.001 < s < 1.5$) Bjerrum and Unmack (1) give the following empirical formulas

$$\left.\begin{array}{ll} 0°\text{C.} & -\log f_{H^+} = 0.192\sqrt{s} - 0.207 \times s - 0.007 \\ 18°\text{C.} & -\log f_{H^+} = 0.166\sqrt{s} - 0.185 \times s - 0.003 \\ 25°\text{C.} & -\log f_{H^+} = 0.161\sqrt{s} - 0.178 \times s - 0.003 \end{array}\right\} \qquad (12)$$

From these formulas we calculate $-\log f_{H^+}$ for the solutions of hydrochloric acid and sodium chloride. For σ we use the value 0.049 (Sörensen, Sörensen, and Linderström-Lang (8)). We find

	At 0°C.	*At 18°C.*	*At 25°C.*
$E \times 10^3$	142.36	150.43	154.25, 154.18
C	4.690	4.662	4.662

It is now easy to calculate K^0 and β from the constants $C + \log K^0$ and $\beta + \sigma$. The results are given in table 3. In order to find K we use the formulas 3, 4, and 12. $-\log K$ is given in the last column of table 2.

SUMMARY

The ratio between the dissociation constants of acetoacetic acid and, respectively, glycolic and acetic acids was determined by means of the quinhydrone electrode at 0 and 18°C. in solutions of sodium chloride up to 0.5 *M*.

The dissociation constants at infinite dilution were computed.

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THE VELOCITY OF BROMINATION OF ACETOACETIC ACID

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Received December 18, 1933

I. INTRODUCTION

In earlier papers (3, 5) the velocity of bromination of acetoacetic ethyl ester was examined. By this reaction we first get α-monobromoacetoacetic ethyl ester, which reacts with more bromine and gives α,α-dibromoacetoacetic ethyl ester. The velocity of bromination is independent of the concentration of bromine. It is a result of the consecutive enolizations of the acetoacetic and monobromoacetoacetic esters, which reactions are catalyzed by bases in general.

In this paper we examine the velocity of bromination of acetoacetic acid in the following solvents: (1) 0.022 to 0.75 *M* hydrochloric acid, (2) solutions of acetoacetic acid and sodium acetoacetate, (3) solutions of glycolic acid and sodium glycolate, and (4) solutions of acetic acid and sodium acetate. In the solutions of hydrochloric acid we first get α-monobromoacetoacetic acid, which reacts with more bromine and gives α,α-dibromoacetoacetic acid. In the three other solvents, where the hydrogen-ion concentration is smaller, the substance is brominated only to α-monobromoacetoacetic acid.

It has been found (6) by electrometric measurements that the dissociation constant of acetoacetic acid at keto-enol equilibrium is 2.62×10^{-4} at 18°C. and 2.57×10^{-4} at 0°C. From the kinetic measurements in hydrochloric acid, it follows that the dissociation constant of α-monobromoacetoacetic acid at 0°C. is about 0.021, that is, eighty times as great as that of acetoacetic acid. By comparison with the dissociation constants of propionic, α-bromopropionic, and α,α-dibromopropionic acids at 25°C., which are 1.34×10^{-5}, 1.08×10^{-3}, and 3×10^{-2}, respectively (8)—ratio 1:81:2200—it is estimated that the dissociation constant of α,α-dibromoacetoacetic acid is of the order 0.6. Acetoacetic and monobromoacetoacetic acid can also split off another proton, viz., in the keto forms at the alpha carbon atom and in the enol forms at the enol group. However, this proton is much more firmly bound than that in the carboxyl group. When we speak of the acetoacetate and monobromoacetoacetate ion or of the dissociation of acetoacetic and monobromoacetoacetic acid, we think only of the dissociation at the carboxyl group.

The degree of enolization of acetoacetic acid in dilute hydrochloric acid at 0°C. is, when equilibrium is attained, 0.7 per cent.

In this paper we shall see that the rate of bromination in the solvents mentioned above may be explained on the following assumptions.

(1) The rate of bromination of the enol forms is very great compared with the rate of enolization of the keto forms. The keto forms are not brominated.

(2) Undissociated acetoacetic and monobromoacetoacetic acid are enolized with measurable velocity. The reactions are catalyzed by bases in general.

(3) The rates of enolization of the acetoacetate and monobromoacetoacetate ions are negligible compared with those of the undissociated acids.

In the solutions of hydrochloric acid, acetoacetic acid is practically completely undissociated. The monobromoacetoacetic acid formed by the reaction is, in the more dilute hydrochloric acid, partly dissociated. The course of the reaction in solutions of hydrochloric acid may be explained by the following scheme, which is analogous to scheme 1a-1d (reference 3) for the bromination of acetoacetic ester.

$$\mathrm{CH_3COCH_2COOH \rightarrow CH_3COH{:}CHCOOH} \tag{1a}$$

$$\mathrm{CH_3COH{:}CHCOOH + Br_2 \rightarrow (CH_3COCHBrCOOH \rightleftarrows CH_3COCHBrCO_2^- + H^+) + H^+ + Br^-} \tag{1b}$$

$$\mathrm{CH_3COCHBrCOOH \rightarrow CH_3COH{:}CBrCOOH} \tag{1c}$$

$$\mathrm{CH_3COH{:}CBrCOOH + Br_2 \rightarrow (CH_3COCBr_2COOH \rightleftarrows CH_3COCBr_2CO_2^- + H^+) + H^+ + Br^-} \tag{1d}$$

The velocity of bromination is determined by the enolizations of acetoacetic acid (1a) and monobromoacetoacetic acid (1c).

In all the other solvents the acetoacetic acid is incompletely dissociated, while the monobromoacetoacetic acid is practically completely dissociated. Therefore the rate of bromination is here determined only by the enolization of the undissociated part of the acetoacetic acid and the basic catalysis of this reaction.

II. EXPERIMENTAL PROCEDURE

Owing to the instability of acetoacetic acid, only fresh solutions of sodium acetoacetate were used. They were prepared by hydrolysis of acetoacetic ethyl ester during the night before the experiments. The acetoacetic ester was purified through the copper compound (3). To a known amount of the ester in a graduated flask was added a small excess of sodium hydroxide. It was diluted to the mark and placed in a thermostat at 18°C. During the night the ester is completely hydrolyzed.

Goldschmidt and Oslan (1) have found that the velocity of hydrolysis is independent of the excess of sodium hydroxide. At 25°C. they found the unimolecular velocity constant $k_1{}^* = 0.008$ (min. $^{-1}$). By an asterisk we denote that the velocity constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343\ k$. In order to find $k_1{}^*$ at 18°C., we assume that the temperature coefficient is the same as for the methyl ester. For the latter Ljunggren (2) found 2.63 for a temperature increase of 10°C. Hence, we calculate for the ethyl ester $k_1{}^* = 0.004$ at 18°C. Consequently, after twelve hours at 18°C. only 0.1 per cent of the ester is not hydrolyzed.

The solutions contained the small amount of ethyl alcohol formed by the hydrolysis. By adding suitable amounts of alcohol it was shown that this has no detectable influence on the bromination.

In a solution of acetoacetic acid a slow ketonic decomposition takes place: $CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$. This reaction has been examined mainly by Widmark (9) and Ljunggren (2). Both the undissociated acid and the ion are decomposed. However the velocity is much greater in acid than in alkaline solution. From experiments of Ljunggren at 37 and 25°C. we calculate the following unimolecular constants for the ketonic decomposition at 18°C.: of the undissociated acetoacetic acid, $k_2{}^* = 1.61 \times 10^{-4}$ (min.$^{-1}$); of the acetoacetate ion, $k_3{}^* = 3.6 \times 10^{-6}$ (min.$^{-1}$).

We denote by c_0 the initial concentration of acetoacetic ester, and by c the sum of the concentrations of the ester and the sodium acetoacetate at the time t minutes after the addition of sodium hydroxide. When the hydrolysis is complete, c is the concentration of sodium acetoacetate. The hydrolysis and ketonic decomposition are consecutive unimolecular reactions with the velocity constants at 18°C. $k_1{}^* = 0.004$ and $k_3{}^* = 3.6 \times 10^{-6}$, respectively. According to Rakowski (7) we may express the course of such reactions by the equation

$$c = c_0 \left[\frac{k_3}{k_3 - k_1} e^{-k_1 t} - \frac{k_1}{k_3 - k_1} e^{-k_3 t} \right]$$

When the hydrolysis is finished $e^{-k_1 t} = 0$ and consequently

$$c = c_0 \frac{k_1}{k_1 - k_3} e^{-k_3 t}$$

If we introduce the values for $k_1{}^*$ and $k_3{}^*$ expressed in hours $^{-1}$, we find that the loss of acetoacetic acid in t hours is $(0.05\ t - 0.1)$ per cent. The concentration, c, of acetoacetate was calculated for each experiment by means of this expression. The solutions were never more than twenty-four hours old when used for the experiments. Consequently less than

1.1 per cent was decomposed. A series of experiments was always carried out within the time of eight hours. During this time the decrease of c is only 0.4 per cent.

The bromination was carried out in the following way. Suitable volumes of water and the slightly alkaline hydrolysis product were measured out and poured into a beaker. To this was added enough potassium bromide solution to make the reacting solution 0.05 *M* with respect to this substance. This was done in order to repress the hydrolysis of the bromine (reference 5, p. 605). The beaker was placed in a water thermostat at 17.94°C. or in a mixture of ice and water. The solution was stirred vigorously with a mechanical stirrer. When temperature equilibrium was nearly attained, either a solution of hydrochloric acid (in the experiments in hydrochloric acid and in solutions of acetoacetic acid and sodium acetoacetate) or a mixture of glycolic acid and sodium glycolate or of acetic acid and sodium acetate was added from a pipet. After a few minutes, when the solution had attained the temperature for the experiment, the reaction was started by sudden addition of bromine water, usually 25 cc. of 0.1 to 0.2 *N*, which was already at the temperature of the experiment. In the experiments at 0°C. the temperature rose a little when bromine water was added. 0.03°C. is therefore used as an average value. The bromination was interrupted by sudden addition of an excess of allyl alcohol, mixed with sufficient hydrochloric acid to make the concentration of this acid at least 0.1 *N* after the experiment. As quickly as possible after the allyl alcohol (2 to 3 seconds), about 1 g. of solid potassium iodide was added. Iodine equivalent with the bromine used by the reaction is slowly liberated. It is titrated with 0.05 *N* sodium thiosulfate. The solutions from the experiments at 0°C. were slowly heated to 18°C. during the titration.

The alkaline sodium acetoacetate solution was acidified as short a time as possible before the start of the bromination, because the ketonic decomposition is much quicker in acid than in alkaline solution. The time from the addition of acid to the end of the bromination was never more than ten minutes. During this time the decomposition is less than 0.4 per cent at 18°C. and less than 0.1 per cent at 0°C., even when the acidity is so great that all the acetoacetic acid is undissociated. The error thus introduced is negligible. The small amount of acetone formed in the alkaline and acid solution does not interfere with the experiment. Acetone reacts with bromine, although more slowly than acetoacetic acid, but the reaction product does not liberate iodine from potassium iodide. During the titration some of the iodine liberated by the bromination products of acetoacetic acid may react with the acetone in the acid solution, but direct experiments with acetone and iodine in hydrochloric acid have shown that this error is of no importance.

The analytical determination of the bromine used by the reaction caused some difficulties. The method is based on the reactions

$$CH_3COCHBrCOOH + 2I^- + H^+ \rightarrow CH_3COCH_2COOH + Br^- + I_2$$

and

$$CH_3COCBr_2COOH + 4I^- + 2H^+ \rightarrow CH_3COCH_2COOH + 2Br^- + 2I_2$$

It was found necessary to have a rather great concentration of hydrochloric acid during the analysis. If the acidity was too small the iodine was liberated too slowly, and the reaction stopped before an equivalent amount of iodine was set free. In the acetate and glycolate mixtures only a fraction of the iodine was liberated in thirty minutes if no hydrochloric acid was added. From this in connection with the increase in velocity, when the hydrogen-ion concentration is increased, we may conclude that the mono- and di-bromoacetoacetate ions react much more slowly with iodide ions than the undissociated acids. When the solution contained at least 0.1 *N* hydrochloric acid the titration could be successfully finished in ten to fifteen minutes.

Another and much more serious difficulty arose. The results of the titration varied with the time between the additions of allyl alcohol and potassium iodide. In order to study the error, this time was varied in otherwise identical experiments. When the bromination took place in hydrochloric acid of different concentration, a decrease of 1 per cent per 3 seconds was found at 18°C. and of 0.1 to 0.3 per cent at 0°C. When the bromination was carried out in acetate mixtures at 18°C., to which was added together with the allyl alcohol enough hydrochloric acid to make it 0.3 *N*, the decrease in bromine was only 0.1 to 0.2 per cent per 3 seconds. From this we conclude that it is hopeless to do experiments in hydrochloric acid at 18°C., while we may consider the error negligible in hydrochloric acid at 0°C. and in acetate and glycolate buffers at 18 and 0°C., provided that the potassium iodide is added not later than 3 seconds after the allyl alcohol. The decrease in titratable bromine is probably caused by a transformation (possibly a ketonic decomposition) of mono- and di-bromoacetoacetic acid into substances which do not react with potassium iodide. The rather slow decrease of titratable bromine in acetate mixtures, where the reaction product is monobromoacetoacetic acid, seems to show that this acid is transformed much more slowly than dibromoacetoacetic acid. Probably the transformation takes place also during the bromination as well as after potassium iodide is added. Although the time of bromination is always very short, and the reaction with potassium iodide rather quick, it is not quite excluded that the error can have some importance. However, the results given later in the paper seem to show that the reaction products are not transformed to any essential degree during the part of the reaction which is used for the calculations.

III. BROMINATION OF ACETOACETIC ACID IN HYDROCHLORIC ACID

Experiments were carried out at 0.03°C. in 0.022 to 0.75 N hydrochloric acid. We shall see that the results agree with the explanation given in the introduction (scheme 1a-1d). According to this the rate of bromination is determined by the consecutive enolizations of the undissociated acetoacetic and monobromoacetoacetic acid (unimolecular constants k_0 and h_0, respectively). The acetoacetic acid (dissociation constant 2.57×10^{-4}) may be considered completely undissociated in all the solutions of hydrochloric acid. At a given concentration of hydrochloric acid a fraction γ' of the monobromoacetoacetic acid is undissociated. If we use the abbreviation $\gamma' h_0/k_0 \equiv r$, and denote by ϵ the degree of enolization of the acetoacetic acid at keto-enol equilibrium, we get for the course of the bromination the following expression, which is analogous to the one found for acetoacetic ester (reference 3, formula 13),

$$\frac{c - \frac{x}{4}}{c} = A\,10^{-k_0^{*}t} - \left(A - 1 + \frac{\epsilon}{2}\right) 10^{-rk_0^{*}t} \tag{3}$$

where c is the initial concentration of acetoacetic acid, x the bromine used by the reaction t minutes after its start in equivalents per liter, and

$$A \equiv (1 - \epsilon)\left(1 + \frac{1}{2(r-1)}\right)$$

It was first shown that the velocity is independent of the concentration of bromine. Hence, the reactions by which bromine is taken up are very rapid compared with those which determine the velocity. It was also shown that $\left(c - \frac{x}{4}\right)\Big/ c$, when t is constant, is independent of the initial concentration of acetoacetic acid. Consequently, the reactions which determine the velocity follow the unimolecular law.

The agreement with formula 3 was shown in a similar way as with acetoacetic ester (3). First ϵ is determined. In another paper (3) it was shown that formula 3 of the present paper, when t is small, may be written

$$\left(c - \frac{x}{4}\right)\Big/ c = 1 - \frac{\epsilon}{2} - t\frac{k_0}{2}[1 + (r - 1)\epsilon]$$

ϵ is small, and r is in the experiments on acetoacetic acid not much different from 1. Hence we have with good approximation, when t is small,

$$\left(c - \frac{x}{4}\right)\Big/ c = 1 - \frac{\epsilon}{2} - \frac{k_0}{2}t \tag{4}$$

In figure 1 $\left(c - \frac{x}{4}\right) \Big/ c$ is plotted against t for all the experiments in solutions of hydrochloric acid, for which $t < 0.2$ min. We shall see later that the mean value of k_0^* for all the solutions of hydrochloric acid is 0.235, which corresponds to $\frac{k_0}{2} = 0.271$. All the points in figure 1 fall close to the straight line with the slope -0.271. If we extrapolate to $t = 0$, we find $\epsilon = 0.0073$.

r is here not much different from 1. It is therefore very difficult to find the values of k_0^* and r which at a given hydrochloric acid concentration give the best agreement between formula 3 and the experiments. We must use the very time-wasting method described previously (reference 3, pp. 754–5). For each pair of values of x and t found by experiment and for a series of values of r we calculate by the method of trial and error the values of k_0^* which satisfy formula 3. In this way we find the values of r for which the variation of k_0^* is smallest. As seen from formula 4, k_0^* is independent of r when t is small. However, we can not determine k_0^* with sufficient accuracy from these experiments. For the determination of k_0^* and r we only use experiments in which $0.94 > \left(c - \frac{x}{4}\right) \Big/ c > 0.5$ (values of k_0^* printed in italics in table 1). Toward the end of the reaction, when $\left(c - \frac{x}{4}\right) \Big/ c < 0.5$, we get a considerable decrease in the value of k_0^*. We always disregard such experiments. The same decrease was found in experiments on acetoacetic ester (3, 5). It may be explained by a consecutive reaction.

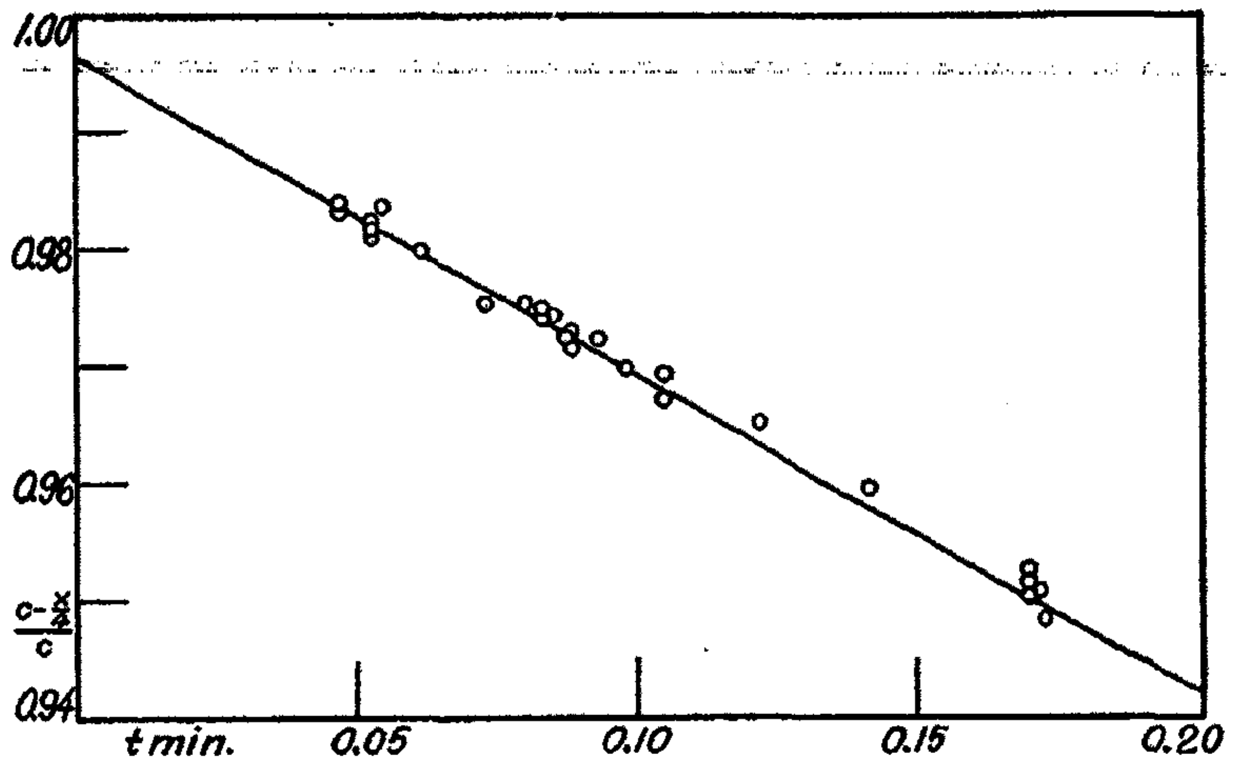

FIG. 1. BROMINATION OF ACETOACETIC ACID IN HYDROCHLORIC ACID

Table 1 contains the experimental results and the calculation of k_0^* and r for a series of experiments in hydrochloric acid. In the eighth column are given the values of $\frac{x}{4}$ calculated from formula 3 when we use the constants given at the top of the table. δ, the difference between $\frac{x}{4}$ found by experiment and calculated from formula 3, is given in the last column. The average deviation $\delta_m = \sqrt{\frac{\Sigma\delta^2}{n-1}}$ where n is the number of experiments, is 2.9×10^{-6}.

TABLE 1

Bromination of acetoacetic acid in (0.0220 M hydrochloric acid + 0.050 M potassium bromide) at 0.03°C.

$\epsilon = 0.0073$; $k_0^* = 0.230$; $r = 0.61$

	$c \times 10^3$	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	k_0^* ($r = 0.50$)	k_0^* ($r = 0.61$)	k_0^* ($r = 0.70$)	$\frac{x}{4} \times 10^3$ (CALCD.)	$\delta \times 10^6$
minutes								
0.047	3.201	0.051	0.9840	0.230	0.230	0.230	0.051	0
0.083	3.209	0.080	0.9750		0.227		0.081	−1
0.122	3.200	0.111	0.9652	0.227	0.226	0.225	0.113	−2
0.170	3.207	0.152	0.9526		0.229		0.153	−1
0.250	2.798	0.189	0.9324	0.231	*0.229*	0.227	0.190	−1
0.670	2.795	0.470	0.8318	0.234	*0.230*	0.226	0.470	0
1.003	2.801	0.681	0.7568	0.238	*0.232*	0.227	0.676	+5
1.503	2.794	0.948	0.6605	0.238	*0.229*	0.223	0.953	−5
2.000	2.799	1.201	0.5710		*0.230*	0.223	1.198	+3
2.337	2.793	1.329	0.5241	0.239	0.227	0.218	1.344	(−15)
3.000	2.796	1.563	0.4410	0.234	0.222		1.602	(−39)

δ_m .... 2.9×10^{-6}

Table 2 gives a summary of eleven series of experiments in hydrochloric acid of different concentrations. The initial hydrogen-ion concentration $(H^+)_0$ is given in the first column. The third column contains the total salt concentration, s. The constants, k_0^* and r, found from the experimental results are given in the fourth and fifth columns. The last column gives the average deviation δ_m, and the last but one the number of experiments, n, used for its calculation. The mean value of δ_m for all the series is 3.3×10^{-6}. The volume during the reaction being 200 cc., this corresponds to 0.05 cc. of 0.05 N thiosulfate. In all the solutions the reaction may be expressed by formula 3 with an accuracy corresponding to the experimental error. The total unsystematic part of the experimental error thus corresponds to an average error of 0.05 cc. on the titration.

The values of k_0^* found for the different solutions of hydrochloric acid are sufficiently constant when we consider the rather small accuracy in the computation of k_0^* and r. The mean value of k_0^* is 0.235. r increases with increasing concentration of hydrochloric acid and attains a constant value 1.15 in the most concentrated solutions. If, as suggested by the explanation given above, only the undissociated part γ' of the monobromoacetoacetic acid is brominated, we find γ' for each of the solutions by dividing r by the constant value of r at great acid concentration. γ' calculated in this way is given in the sixth column of table 2.

According to scheme 1 hydrogen ions are formed by the reaction. In the second column of table 2 is given $(H^+)_m$, a mean value of the hydrogen-ion concentration. If the explanation holds $\frac{1-\gamma'}{\gamma'}$ $(H^+)_m$ is the dissociation constant, K, of monobromoacetoacetic acid. K is given in the seventh column of table 2. Although the values of r are only rough, and the salt concentration, s, varies from 0.074 to 0.80, K is nearly constant. The average value is 0.021, eighty times as great as the dissociation constant of acetoacetic acid. This value is reasonable as seen from the following comparison. The ratio between the dissociation constants of monobromoacetic and acetic acids at 25°C. is $1.38 \times 10^{-3}/1.77 \times 10^{-5} = 77:1$, and that between the constants for α-monobromopropionic and propionic acids is $1.08 \times 10^{-3}/1.34 \times 10^{-5} = 81:1$.

TABLE 2

Bromination of acetoacetic acid in hydrochloric acid at 0.08°C.

KBr, 0.050 *M*. NaCl, 0.004 *M* (except in the series marked †, which contains NaCl, 0.304 *M*)

$(H^+)_s$	$(H^+)_m$	s	k_0^*	r	γ'	K	n	$\delta_m \times 10^6$
0.0220	0.0238	0.074	0.230	0.61	0.53	0.021	9	2.9
0.0260	0.0280	0.078	0.234	0.69	0.60	0.019	9	3.0
0.0337	0.0357	0.086	0.238	0.71	0.62	0.022	8	4.3
†0.0337	0.0356	0.386	0.226	0.66	0.57	(0.027)	9	4.1
0.0459	0.0480	0.098	0.239	0.80	0.70	0.021	8	3.5
0.0966	0.0986	0.149	0.240	0.92	0.80	0.025	8	2.3
0.120	0.122	0.172	0.240	1.00	0.87	0.018	11	2.9
0.247	0.249	0.300	0.240	1.06	0.92	0.022	7	4.0
0.37	0.37	0.42	0.238	1.10	0.96	0.02	11	2.9
0.50	0.50	0.55	0.234	1.15	1.00		7	3.2
0.75	0.75	0.80	0.228	1.15	1.00		7	3.0

Mean values: $k_0^* = 0.235$, $h_0^* = 0.27$, $K = 0.021$, $\delta_m = 3.3 \times 10^{-6}$.

$r = 1.15$, when $\gamma' = 1$. Hence the velocity constant for the enolization of undissociated monobromoacetoacetic acid at 0°C. is $h_0^* = 1.15 \times 0.235 = 0.27$.

IV. BROMINATION OF SOLUTIONS OF ACETOACETIC ACID AND SODIUM ACETOACETATE

In this chapter the rate of bromination was studied at 0 and 18°C. in solutions containing both acetoacetic acid and sodium acetoacetate. According to the explanation given before, the rate is determined by the enolizations of the undissociated forms of acetoacetic and monobromoacetoacetic acids, which reactions are catalyzed by bases. In the preceding chapter it was found that the velocity constants for the enolizations of the two acids, when no catalyst is added, are of the same order of magnitude. This probably also holds for the catalyzed reactions. In the acetoacetic acid–sodium acetoacetate mixtures the hydrogen-ion concentration is so small that the monobromoacetoacetic acid is practically completely dissociated. Consequently, this is not further brominated during the experiment. The velocity is determined only by the enolization of undissociated acetoacetic acid, which proceeds by two simultaneous reactions, the "uncatalyzed" water reaction with the velocity constant k_0 and the reaction catalyzed by the acetoacetate ion (catalytic constant k_{R^-}). Hence, we may express the velocity by the differential equation

$$\frac{\mathrm{d}\frac{x}{2}}{\mathrm{d}t} = k_0(\mathrm{HR}) + k_{\mathrm{R}^-}(\mathrm{R}^-)(\mathrm{HR}) \tag{6}$$

According to scheme 1b hydrogen ions are produced by the bromination. The gross reaction is

$$\mathrm{CH_3COCH_2COOH + Br_2 + 2CH_3COCH_2CO_2^- \rightarrow CH_3COCHBrCO_2^- + Br^-} \\ \mathrm{+\ 2CH_3COCH_2COOH}$$

or

$$\mathrm{2CH_3COCH_2CO_2^- + Br_2 \rightarrow CH_3COCHBrCO_2^- + CH_3COCH_2COOH + Br^-} \tag{7}$$

It is the object of the following examination to show that the velocity of bromination agrees with equation 6 and scheme 7. In addition, we shall determine the constants k_0 and k_{R^-}. Thus, k_0 is here found independently of the determination in the last chapter.

The initial stoichiometric concentrations of acetoacetic acid and sodium acetoacetate are denoted by $c - b$ and b, respectively. At the start of the bromination we have $(\mathrm{HR}) = c - b - (\mathrm{H}^+)$ and $(\mathrm{R}^-) = b + (\mathrm{H}^+)$. According to scheme 7 we have at the time t

$$(\mathrm{HR}) = c - b + \frac{x}{2} - (\mathrm{H}^+) \tag{8}$$

$$(\mathrm{R}^-) = b - x + (\mathrm{H}^+) \tag{9}$$

(H^+) increases considerably during the reaction.

In each experiment within a series we have determined a pair of values of x and t. We first calculate (H^+) corresponding to each value of x in the series by means of expressions 8 and 9 and

$$(H^+) = \frac{(HR)}{(R^-)} K_{HR} \tag{10}$$

For the dissociation constant K_{HR} of acetoacetic acid we use the values which have been determined electrometrically at 0 and 18°C. in solutions of sodium chloride (6).

We now know for each experiment in the series values of x, (HR), (R^-), and t. The object is to determine such values of k_0 and k_{R^-} that equation 6 is satisfied for all the experiments. By numerical integration of the curves which we obtain by plotting (HR) and the product $(HR)(R^-)$ against t, we find values of the integrals

$$I_0 \equiv \int_{t_1}^{t} (HR)\, dt \quad \text{and} \quad I_{R^-} \equiv \int_{t_1}^{t} (HR)(R^-)\, dt \tag{12}$$

We denote by $\Delta\left(\frac{x}{2}\right)$, ΔI_0, and ΔI_{R^-} the increases of $\frac{x}{2}$, I_0, and I_{R^-} when going from the m^{th} to the n^{th} experiment in a series. Hence, equation 6 may be written

$$\Delta\left(\frac{x}{2}\right) = k_0 \Delta I_0 + k_{R^-} \Delta I_{R^-} \tag{14}$$

or

$$\frac{\Delta\left(\frac{x}{2}\right)}{\Delta I_{R^-}} = k_{R^-} + k_0 \frac{\Delta I_0}{\Delta I_{R^-}} \tag{15}$$

The change of $\frac{\Delta I_0}{\Delta I_{R^-}}$ when going from one pair of experiments to another within a series, is so small that we cannot get a good determination of k_0 and k_{R^-} from a single series without knowing one of them. However we can get this by combining all the series at a certain temperature. In the different series we have mainly varied the concentration c. In the experiments with the smallest c, the catalytic reaction plays a subordinate part. Here $k_{R^-}\Delta I_{R^-}$ is small compared with $k_0 \Delta I_0$. In the experiments with the greatest c, the catalytic reaction is of especially great importance. Here $k_{R^-}\Delta I_{R^-} > k_0 \Delta I_0$. When we compute one pair of values of k_0 and k_{R^-} from all the experiments at constant temperature, we must naturally assume that the constants are the same in all the solvents used. The salt concentration only varies from 0.056 to 0.087 M. It is consequently excluded that the change in primary salt effect can be important. Equations 15 are solved graphically by plotting $\Delta\left(\frac{x}{2}\right) \Big/ \Delta I_{R^-}$ against $\Delta I_0/\Delta I_{R^-}$ for all the experiments (figure 2). Although the velocity, especially at 18°C., is so great that it is difficult to follow the reaction, the points fall close along straight lines, which determine the constants k_0 and k_-. We find

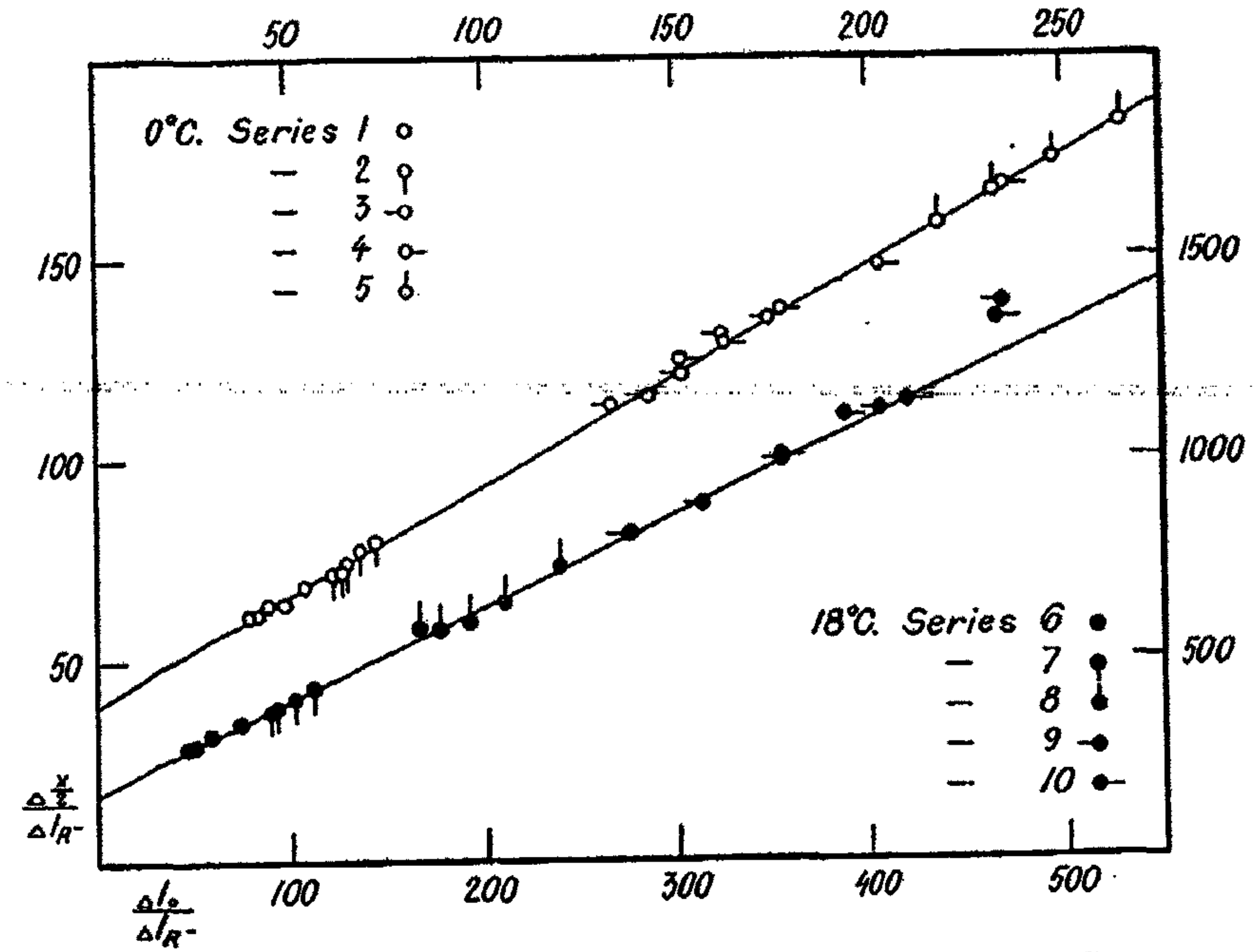

FIG. 2. BROMINATION OF SOLUTIONS OF ACETOACETIC ACID AND SODIUM ACETOACETATE

Coördinates at the top and to the left are for the experiments at 0°C.; those at the bottom and to the right are for the experiments at 18°C.

t	k_0	k_{R^-}	k_0^*	$k_{R^-}^*$
degrees C.				
0.03	0.544	38.8	0.236	16.9
17.94	2.30	172	0.999	74.7

In table 3 is given the composition of the solutions in ten series of experiments, five at each temperature. Table 4 gives the experimental data for series 1. In order to test how well the experiments agree with equation 14 when the values of k_0 and k_{R^-} are introduced, we calculate from this

TABLE 3

Bromination of solutions of acetoacetic acid and sodium acetoacetate

All the solutions contained KBr, 0.050 *M*

TEMPERATURE	SERIES	$b \times 10^3$	$c \times 10^3$	(NaCl)	s	$K_{HR} \times 10^4$	k_0	k_{R^-}
degrees C.								
0.03	1	29.06	33.63	0.008	0.087	4.0	0.544	38.8
	2	17.81	19.84	0.004	0.072	3.9		
	3	8.57	10.48	0.003	0.062	3.8		
	4	7.508	8.515	0.002	0.059	3.8		
	5	4.882	5.373	0.001	0.056	3.7		
17.94	6	26.43	29.45	0.006	0.082	4.0	2.30	172
	7	13.65	14.89	0.003	0.067	3.9		
	8	7.283	8.300	0.002	0.059	3.8		
	9	4.629	5.298	0.001	0.056	3.8		
	10	3.778	4.554	0.002	0.056	3.8		

TABLE 4

Bromination of solutions of acetoacetic acid and sodium acetoacetate at 0.03°C.

Series 1

NO.	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\frac{x}{2} \times 10^3$ (CALCD.)	$\delta \times 10^3$	$(H^+) \times 10^3$	$(HR) \times 10^3$	$(R^-) \times 10^3$	$(HR)(R^-) \times 10^6$	$l_0 \times 10^3$	$l_{R^-} \times 10^6$
	minutes									
1	0.062	0.61	0.63	−0.02	0.07	5.14	27.91	143.5	0.000	0.00
2	0.100	0.96	0.95	+0.01	0.08	5.50	27.22	149.7	0.202	5.57
3	0.168	1.58	1.58	0.00	0.09	6.10	25.99	158.5	0.597	16.05
4	0.255	2.45	2.44	+0.01	0.11	6.92	24.27	167.9	1.163	30.27
5	0.333	3.28	3.27	+0.01	0.14	7.72	22.64	174.8	1.734	43.65
6	0.425	4.31	4.31	0.00	0.17	8.71	20.61	179.5	2.490	59.98
7	0.503	5.20	5.25	+0.04	0.21	9.68	18.69	180.9	3.207	74.06
8	0.583	6.18	6.25	−0.07	0.25	10.49	16.95	177.8	4.014	88.44
9	0.667	7.35	7.32	+0.03	0.32	11.57	14.68	169.8	4.940	103.05

NO.	$\Delta\left(\frac{x}{2}\right) \times 10^3$	$\Delta l_0 \times 10^3$	$\Delta l_{R^-} \times 10^6$	$\frac{\Delta\left(\frac{x}{2}\right)}{\Delta l_{R^-}}$	$\frac{\Delta l_0}{\Delta l_{R^-}}$
5-1	2.67	1.734	43.65	61.2	39.7
6-2	3.35	2.288	54.41	61.6	42.1
7-3	3.71	2.610	58.01	64.0	45.0
8-4	3.73	2.851	58.17	64.1	49.0
9-5	4.07	3.206	59.40	68.5	54.0

equation $\Delta\left(\frac{x}{2}\right)$, when going from the first to each of the other experiments in the series. In order to calculate $\frac{x}{2}$ we might assume that experiment No. 1 has no error, but it is more reasonable to calculate $\frac{x}{2}$ from the assumption that the algebraic sum of the errors is as near 0 as possible. The values in the fourth column of table 4 have been found in this way. The fifth column gives δ, the difference between the experimental and calculated value of $\frac{x}{2}$. It is seen that the agreement is good.

TABLE 5

Bromination of solutions of acetoacetic acid and sodium acetoacetate

Series 2 to 10

SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$	SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$	SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$
	minutes				*minutes*				*minutes*		
2	0.047	0.234	+0.006	5	0.058	0.039	−0.002	8	0.057	0.295	−0.037
	0.105	0.404	+0.014		0.307	0.139	0.000		0.087	0.469	0.000
	0.205	0.681	−0.010		0.500	0.227	+0.001		0.120	0.664	+0.029
	0.307	1.005	−0.021		0.697	0.324	−0.002		0.155	0.837	+0.011
	0.403	1.366	−0.004		0.997	0.502	0.000		0.190	1.029	−0.007
	0.503	1.747	−0.013		1.258	0.682	+0.003		0.223	1.245	−0.001
	0.608	2.173	−0.007		1.500	0.863	−0.003		0.270	1.572	0.000
	0.703	2.613	+0.006						0.307	1.841	−0.008
	0.803	3.113	+0.026						0.360	2.283	+0.011
3	0.053	0.138	−0.007	6	0.043	1.16	−0.06	9	0.053	0.157	−0.011
	0.205	0.426	+0.006		0.073	2.11	+0.03		0.142	0.403	+0.001
	0.310	0.615	−0.010		0.092	2.65	−0.04		0.205	0.593	−0.005
	0.407	0.811	−0.013		0.137	4.28	−0.03		0.257	0.787	+0.005
	0.503	1.041	+0.008		0.168	5.61	+0.06		0.297	0.937	+0.002
	0.608	1.273	−0.001		0.208	7.28	+0.01		0.357	1.181	−0.006
	0.705	1.495	−0.012		0.240	8.72	+0.05		0.407	1.412	−0.001
	0.807	1.777	+0.013						0.453	1.649	+0.014
	0.900	2.019	+0.013						0.497	1.952	(+0.095)
4	0.060	0.081	−0.015	7	0.047	0.403	−0.001	10	0.107	0.313	−0.011
	0.202	0.226	0.000		0.057	0.479	+0.001		0.150	0.446	−0.004
	0.320	0.341	−0.004		0.108	0.908	+0.006		0.185	0.566	+0.004
	0.500	0.537	−0.006		0.150	1.336	+0.022		0.223	0.670	−0.021
	0.753	0.869	+0.007		0.227	2.180	−0.033		0.257	0.811	−0.003
	1.000	1.229	+0.007		0.253	2.537	−0.023		0.290	0.954	+0.014
	1.250	1.638	+0.004		0.287	3.052	+0.006		0.320	1.063	+0.004
	1.505	2.094	−0.006		0.320	3.577	+0.025		0.353	1.213	+0.018
	1.747	2.595	+0.014								

In table 5 is given a short survey of the nine other series of experiments.

In the last chapter we found $k_0^* = 0.235$, which is a mean value of eleven series of experiments on the bromination of acetoacetic acid in solutions of hydrochloric acid at 0°C. This is in good agreement with the value $k_0^* = 0.236$ found in this chapter. It may be mentioned that the calculation of the experiments in hydrochloric acid was completed before the calculation of the experiments in this chapter.

V. BROMINATION OF ACETOACETIC ACID IN GLYCOLATE AND ACETATE BUFFER SOLUTIONS

The hydrogen-ion concentration of the solutions used in this chapter is so small that only a rather small part of the acetoacetic acid is undissociated, and the monobromoacetoacetic acid formed by the bromination is completely dissociated. In agreement with the explanation given in the introduction, the velocity of bromination is determined only by the enolization of the undissociated acetoacetic acid, which reaction is catalyzed by bases. The reaction product, monobromoacetoacetic acid, is not further brominated. If the solution contains the weak acid HB and its sodium salt NaB, the velocity is determined by the differential equation

$$\frac{d\left(\frac{x}{2}\right)}{dt} = k_0(\mathrm{HR}) + k_{\mathrm{R^-}}(\mathrm{R^-})(\mathrm{HR}) + k_{\mathrm{B^-}}(\mathrm{B^-})(\mathrm{HR}) \qquad (16)$$

where $k_{\mathrm{B^-}}$ is the catalytic constant for the base $\mathrm{B^-}$.

By the bromination of one molecule of acetoacetic acid to the monobromoacetoacetate ion, two hydrogen ions are set free

$$\mathrm{CH_3COCH_2COOH + Br_2 \rightarrow CH_3COCHBrCO_2^- + Br^- + 2H^+} \qquad (17)$$

We shall see that the experiments in glycolate and acetate buffer solutions at 0 and 18°C. agree with equation 16 and scheme 17. In addition, we shall determine the catalytic constants of glycolate and acetate ions.

The buffer solutions were prepared from glycolic or acetic acid and sodium hydroxide as previously described (5). The volume during the bromination was always 200 cc. We use the following notations for the stoichiometric concentrations. c is the total concentration of undissociated and dissociated acetoacetic acid at the beginning of the experiment. $c = (\mathrm{HR}) + (\mathrm{R^-})$, when $t = 0$. g is the total concentration of the acid HB and its salt NaB. $g = (\mathrm{HB}) + (\mathrm{B^-})$. b is the total concentration (referred to the volume during the bromination) of the sodium hydroxide used for the preparation of the amount of buffer solution and alkaline sodium acetoacetate solution taken for the experiment. $b = (\mathrm{R^-}) + (\mathrm{B^-}) - (\mathrm{H^+})$, when $t = 0$.

At the time t we have

$$(\mathrm{HR}) + (\mathrm{R}^-) = c - \frac{x}{2} \tag{18}$$

and

$$(\mathrm{HB}) + (\mathrm{B}^-) = g \tag{19}$$

$$(\mathrm{R}^-) + (\mathrm{B}^-) - (\mathrm{H}^+) = b - x \tag{20}$$

We denote by γ_0, γ, and γ_∞ the fractions of the acetoacetic acid which are undissociated at the times 0, t, and ∞, respectively. We use the abbreviation

$$\gamma_m = \tfrac{1}{2}(\gamma_0 + \gamma_\infty) \tag{21}$$

From equations 18 to 20 and

$$(\mathrm{HR}) = \gamma\left(c - \frac{x}{2}\right) \tag{22}$$

we get

$$(\mathrm{R}^-) = (1 - \gamma)\left(c - \frac{x}{2}\right) \tag{23}$$

$$(\mathrm{HB}) = g - b - (\mathrm{H}^+) + c(1 - \gamma) + \frac{x}{2}(1 + \gamma) \tag{24}$$

and

$$(\mathrm{B}^-) = b + (\mathrm{H}^+) - c(1 - \gamma) - \frac{x}{2}(1 + \gamma) \tag{25}$$

If we denote by L the ratio between the dissociation constants of acetoacetic acid and the acid HB

$$L = K_{\mathrm{HR}}/K_{\mathrm{HB}} \tag{26}$$

we have

$$\gamma = \frac{(\mathrm{HB})}{L(\mathrm{B}^-) + (\mathrm{HB})}$$

By introducing equations 24 and 25 we obtain

$$\gamma = \frac{g - b - (\mathrm{H}^+) + c(1 - \gamma) + \frac{x}{2}(1 + \gamma)}{g + (L - 1)[b + (\mathrm{H}^+) - c(1 - \gamma) - \frac{x}{2}(1 + \gamma)]} \tag{27}$$

$$\gamma_0 = \frac{g - b - (\mathrm{H}^+) + 2c - (1 + \gamma_0)c}{g + (L - 1)(b + (\mathrm{H}^+) - 2c) + (L - 1)(1 + \gamma_0)c} \tag{28}$$

and

$$\gamma_\infty = \frac{g - b - (\mathrm{H}^+) + 2c}{g + (L - 1)(b + (\mathrm{H}^+) - 2c)} \tag{29}$$

The hydrogen-ion concentration increases so little during the bromination that it is sufficiently accurate to use an average value calculated from the expression

$$(\mathrm{H}^+) = K_{\mathrm{HR}} \frac{\gamma_m}{1-\gamma_m} \tag{30}$$

In order to calculate γ_0, γ_∞, γ_m, and (H^+) from the expressions 28, 29, 21, and 30, we proceed in the following way. We first calculate approximate values of γ_0 and γ_∞ by setting $(\mathrm{H}^+) = 0$ and $\gamma_0 = 0$ on the right side of equations 28 and 29. In another paper (6) L has been determined electrometrically in solutions of varying salt concentration, s. By means of equation 21 we now find a preliminary value of γ_m, which we introduce into equation 30. In this way we get a sufficiently good value of (H^+). γ_∞ is now calculated from equation 29. By introducing the preliminary value of γ_0 on the right side of equation 28 we find a better value of γ_0, and continue in the same way until a repetition gives the same value. From the final values of γ_0 and γ_∞ we calculate the mean value γ_m.

If we use the abbreviations

$$f_0 \equiv \frac{k_0}{k_{\mathrm{B}^-}} \quad \text{and} \quad f_{\mathrm{R}^-} \equiv \frac{k_{\mathrm{R}^-}}{k_{\mathrm{B}^-}} \tag{31}$$

the differential equation 16 may be written in the following way

$$\frac{\mathrm{d}\left(\frac{x}{2}\right)}{\mathrm{d}t} = k_{\mathrm{B}^-}(\mathrm{HR})\,[f_0 + f_{\mathrm{R}^-}(\mathrm{R}^-) + (\mathrm{B}^-)] \tag{32}$$

If we introduce equations 22, 23, and 25, we get

$$\frac{\mathrm{d}\left(\frac{x}{2}\right)}{\mathrm{d}t} = k_{\mathrm{B}^-}\gamma\left(c - \frac{x}{2}\right)\left[f_0 + b + (\mathrm{H}^+) - (1 - f_{\mathrm{R}^-})\,(1-\gamma)c - (1 + \gamma + (1-\gamma)\,f_{\mathrm{R}^-})\frac{x}{2}\right] \tag{33}$$

For the first γ in this equation we introduce expression 27. In the equation thus obtained we use for γ the approximate value γ_m. We use the abbreviations

$$E \equiv \frac{g - b - (\mathrm{H}^+) + 2c}{1+\gamma_m} - c \tag{34}$$

$$F \equiv \frac{b + (\mathrm{H}^+) + f_0 - (1 - f_{\mathrm{R}^-})(1-\gamma_m)c}{(1+\gamma_m) + (1-\gamma_m)\,f_{\mathrm{R}^-}} \tag{35}$$

$$G \equiv \frac{g + (L-1)\,(b + (\mathrm{H}^+) - (1-\gamma_m)c)}{(L-1)\,(1+\gamma_m)} \tag{36}$$

The differential equation 33 may now be written

$$\frac{\mathrm{d}\left(\frac{x}{2}\right)}{\mathrm{d}t} = k_{\mathrm{B}^-} \frac{1 + \gamma_m + (1 - \gamma_m) f_{\mathrm{R}^-}}{L - 1} \, \frac{\left(c - \frac{x}{2}\right)\left(E + \frac{x}{2}\right)\left(F - \frac{x}{2}\right)}{\left(G - \frac{x}{2}\right)} \tag{37}$$

We integrate equation 37 and introduce $\frac{x}{2} = c(\gamma_0 \epsilon + (1 - \gamma_0)\epsilon_i)$, when $t = 0$, where ϵ and ϵ_i are the degrees of enolization at keto-enol equilibrium of undissociated acetoacetic acid and the acetoacetate ion respectively. $c(\gamma_0 \epsilon + (1 - \gamma_0)\epsilon_i)$ is negligible compared with E and F. We thus get

$$S + k^* t = f(x) \tag{38}$$

where we have used the following abbreviations

$$f(x) \equiv \log \frac{c}{c - \frac{x}{2}} + \Delta_1 - \Delta_2 \tag{39}$$

$$\Delta_1 \equiv M \log \frac{E + \frac{x}{2}}{E} \tag{40}$$

$$\Delta_2 \equiv N \log \frac{F}{F - \frac{x}{2}} \tag{41}$$

$$k \equiv \gamma_\infty \left[k_0 + k_{\mathrm{B}^-}(\mathrm{B}^-)_{t=\infty}\right] \tag{42}$$

$$M \equiv P \frac{g(b + (\mathrm{H}^+) - 2c + f_0)}{g + (L - 1)(b + (\mathrm{H}^+) - 2c)} \tag{43}$$

$$N \equiv (1 - f_0 P)\gamma_\infty \tag{44}$$

$$P \equiv \frac{(1 + \gamma_m)L}{(1 + \gamma_m)(g + f_0) + (1 - \gamma_m) f_{\mathrm{R}^-}(g - b - (\mathrm{H}^+) + 2c)} \tag{45}$$

$$S \equiv -\log\left(1 - \gamma_0 \epsilon - (1 - \gamma_0)\epsilon_i\right) \tag{46}$$

In order to show that the experiments agree with formula 38, we proceed in the following way. The composition of the solution within a series of experiments is given by g, b, c, and the total salt concentration s. We first calculate L from formulas 11 (reference 6). We then calculate γ_0, γ_∞, γ_m, and (H^+) from expressions 28, 29, 21, and 30 as explained before. Δ_1 and Δ_2 in formula 39 are rather small compared with $\log \frac{c}{c - \frac{x}{2}}$. We may therefore find an approximate value of k^* from the slope of the straight line which we get by plotting $\log \frac{c}{c - \frac{x}{2}}$ against t. When we use the values of k_0^* and $k_{R^-}^*$ found in the last chapter and the rough value of k^* found here, we calculate by means of expressions 42 and 31 approximate values of f_0 and f_{R^-}. From these values we calculate by means of expressions 34 to 36, 39 to 41, and 43 to 45 approximate values of $f(x)$, which we plot against t. In this way we find a better value of k^*. We repeat the computation, and continue until a repetition gives the same value of k^*. We now find $k_{B^-}^*$ from equation 42. S is the intercept on the ordinate axis of the straight line we get by plotting $f(x)$ against t.

TABLE 6

Bromination of acetoacetic acid in a mixture of glycolic acid and sodium glycolate at 0.03°C.

$g = 0.09285$ $b = 0.07802$ $c = 0.003084$ $(KBr) = 0.050$
$(C_2H_5OH) = 0.0031$ $s = 0.128$ $L = 1.862$ $(H^+) = 0.00006$
$\gamma_\infty = 0.1353$ $\gamma_0 = 0.1110$ $\gamma_m = 0.1232$ $f_0 = 0.0124$
$f_{R^-} = 0.89$ $E = 0.01557$ $F = 0.04737$ $M = 0.787$
$N = 0.115$ $k^* = 0.2211$ $k_{B^-}^* = 19.4$ $S = 0.0021$

t	$\frac{x}{2} \times 10^3$	$\log \frac{c}{c - \frac{x}{2}}$	Δ_1	Δ_2	$f(x)$ (EXPTL.)	$f(x)$ (CALCD.)	$\delta \times 10^4$	$\delta_t \times 10^3$
minutes								
0.067	0.107	0.0153	0.0024	0.0001	0.0176	0.0169	+7	+3
0.337	0.436	0.0662	0.0095	0.0005	0.0752	0.0766	−14	−6
0.670	0.817	0.1338	0.0175	0.0009	0.1504	0.1502	+2	+1
1.003	1.146	0.2016	0.0243	0.0012	0.2247	0.2239	+8	+4
1.335	1.419	0.2681	0.0298	0.0015	0.2964	0.2973	−9	−4
1.668	1.668	0.3380	0.0348	0.0018	0.3710	0.3709	+1	0
1.998	1.866	0.4047	0.0387	0.0020	0.4414	0.4430	(−25)	(−11)

The results of two series of experiments are given in tables 6 and 7. Table 8 gives a survey of six series in glycolate buffers and fourteen series in acetate buffers. The sixth column in tables 6 and 7 contains $f(x)$ found from the experiments. The seventh column gives $f(x)_{\text{calcd.}} = k^*t + S$, calculated for all the values of t and the values of k^* and S found in the series. The experiments agree well with formula 38. This is seen from the next to the last column, where $\delta = f(x) - f(x)_{\text{calcd.}}$ is given. δ is usually small. Only when much more than half of the acetoacetic acid is brominated may we get a considerable deviation. A disappearance of titratable bromine also takes place here, although at a much later stage than in hydrochloric acid. This is seen from table 7. Here the experiments still agree with the formula when 73 per cent of the reaction has taken place (t = 0.353). While the titratable bromine at the time t = 2 corresponds to 99 per cent of the acetoacetic acid, it has at the time t = 5 fallen to 80 per cent.

The velocity is often so great that it is difficult to follow the reaction. Thus the time of half-completion varies from 6 to 22 seconds in the experiments at 18°C. Probably a considerable part of the unsystematic error is due to errors in the determination of the time when the reaction is started and stopped. When we introduce into formula 38 the values of k^* and S found in a series of experiments, we may calculate t for each of the experimental values of $f(x)$. The difference δ_t between the experimental and calculated values of t may also be found from the expression

TABLE 7

Bromination of acetoacetic acid in a mixture of acetic acid and sodium acetate at 17.94°C.

$g = 0.2018$ $b = 0.1042$ $c = 0.003083$ $(\mathrm{KBr}) = 0.050$
$(\mathrm{C_2H_5OH}) = 0.0031$ $s = 0.154$ $L = 14.62$ $(\mathrm{H^+}) = 0.0000$
$\gamma_\infty = 0.06759$ $\gamma_0 = 0.06353$ $\gamma_m = 0.06556$ $f_0 = 0.0043$
$f_{\mathrm{R^-}} = 0.322$ $E = 0.0943$ $F = 0.0780$ $M = 0.835$
$N = 0.0495$ $k^* = 1.602$ $k_{\mathrm{B^-}}^* = 232$ $S = 0.0059$

t	$\frac{x}{2} \times 10^3$	$\log \frac{c}{c - \frac{x}{2}}$	Δ_1	Δ_2	$f(x)$ (EXPTL.)	$f(x)$ (CALCD.)	$\delta \times 10^4$	$\delta_t \times 10^3$
minutes								
0.053	0.571	0.0889	0.0022	0.0002	0.0909	0.0908	+1	0
0.097	0.943	0.1587	0.0036	0.0003	0.1620	0.1613	+7	0
0.120	1.118	0.1955	0.0043	0.0003	0.1995	0.1981	+14	+1
0.162	1.384	0.2587	0.0053	0.0004	0.2636	0.2654	−18	−1
0.203	1.629	0.3257	0.0063	0.0005	0.3315	0.3311	+4	0
0.353	2.238	0.5625	0.0085	0.0006	0.5704	0.5714	−10	−1
1.003	3.030	1.790	0.0114	0.0009	1.800	1.613		
2.000	3.054	2.074	0.0115	0.0009	2.085	3.210		
5.000	2.47							

$\delta_t = \delta/k^*$. δ_t is given in the last column of tables 6 and 7. The average deviation for all the experiments has been calculated from the formula $\delta_{tm} = \sqrt{\frac{\Sigma\delta_t^2}{n-1}}$, where n is the number of experiments. In the calculation we have omitted experiments where more than 60 per cent of the reaction has taken place, because in the last part of the reaction great deviations of another origin are found. In this way we find from ninety experiments δ_{tm} = 0.0026 minute or 0.15 second. From table 8 we see that $k_{\mathrm{B^-}}^*$ is, to a good approximation, constant at constant temperature for each of the catalysts.

In each series we have determined the constant S (expression 46). Owing to the great velocity the value is very rough. If we calculate ϵ_i, the degree of enolization of the acetoacetate ion, from S found in the experiments at 0°C. and $\epsilon = 0.0073$, we get the values given in the last column of table 8. The mean value of thirteen determinations is $\epsilon_i = 0.0045$ with an average error of 0.0005. In spite of the rather small unsystematic error, we take reservation for the reliability of this value.

TABLE 8

Bromination of acetoacetic acid in glycolate and acetate buffer solutions

All solutions contain KBr, 0.050 M

BUFFER	TEMPERATURE	$c \times 10^3$	s	$(HB)_{t=\infty}$	$(B^-)_{t=\infty}$	γ_0	γ_∞	k^*	$k_{B^-}^*$	$\epsilon_i \times 10^4$
	degrees C.									
Glycolate	0.03	3.08	0.128	0.02094	0.0719	0.1110	0.1353	0.2211	19.4	45
		2.87	0.129	0.02344	0.0729	0.1250	0.1472	0.2429	19.4	42
		2.87	0.204	0.0446	0.1484	0.1292	0.1403	0.4279	19.0	48
		2.87	0.204	0.0832	0.1484	0.2218	0.2334	0.722	19.3	38
		2.87	0.204	0.1220	0.1484	0.2969	0.3085	0.956	19.3	52
	17.94	2.87	0.129	0.02344	0.0729	0.1326	0.1564	1.084	81.4	
Acetate	0.03	3.34	0.154	0.0517	0.0973	0.02981	0.03293	0.1844	55.1	50
		3.33	0.104	0.0520	0.0475	0.05802	0.06626	0.1881	54.8	44
		3.33	0.154	0.1013	0.0973	0.05856	0.06257	0.3478	54.7	54
		6.66	0.158	0.1041	0.0945	0.05760	0.06584	0.3631	55.9	42
		3.33	0.254	0.2003	0.1976	0.05776	0.05972	0.6552	54.3	39
		3.34	0.154	0.2006	0.0973	0.1109	0.1167	0.6478	54.6	42
		3.33	0.104	0.2016	0.0473	0.1995	0.2161	0.6151	55.1	40
		6.65	0.108	0.2044	0.0445	0.1945	0.2287	0.6270	56.3†	
		3.33	0.254‡	0.2016	0.0474	0.2022	0.2106	0.6011	55.3	48
	17.94	3.08	0.104	0.0514	0.0475	0.06086	0.06891	0.814	228	
		3.08	0.104	0.0528	0.0477	0.06232	0.07044	0.878	240	
		3.09	0.154	0.1005	0.0980	0.06160	0.06556	1.538	229	
		3.08	0.154	0.1038	0.0980	0.06353	0.06759	1.602	232	
		3.08	0.254	0.1978	0.1978	0.06206	0.06401	3.01	233	

Mean values of $k_{B^-}^*$: Glycolate catalysis, 19.3 at 0.03°C, 81.4 at 17.94°C. Acetate catalysis, 55.0 at 0.03°C., 232 at 17.94°C.

† Omitted, when taking the mean value, because the series is considered less accurate.

‡ Containing NaCl, 0.150 M.

VI. GENERAL BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ACID

All the experimental evidence on the bromination of acetoacetic acid to α-monobromoacetoacetic acid confirms the assumption that the velocity of this reaction is determined by the enolization of the undissociated part of the acetoacetic acid, which reaction is catalyzed by bases in general. No acid catalysis was found. The theory of general basic catalysis and prototropic isomerization was discussed in another paper (4), where references to the literature may be found. According to the theory the velocity of enolization is determined by the velocity with which the proton in the alpha position to the carboxyl group is transferred to the basic catalyst. We found by experiment that the enolization of the ions of acetoacetic and monobromoacetoacetic acids is very slow in comparison with that of the undissociated acids. This is in agreement with the theory because the proton, owing to the free negative charge, is bound much more firmly in the ions than in the neutral acids. When the basic catalyst has a negative charge the electrostatic repulsion will further counteract the reaction of the ion.

TABLE 9

Basic catalysis of the enolization of acetoacetic acid at 0 and 18°C.

$\beta = 0.50$

TEMPERATURE	CATALYST	p	q	K^c_{HB}	$\log\left(\frac{p}{q}K^\circ_B\right)$	$k_{B^-}^*$	$\log\left(\frac{1}{q}k_{B^-}^*\right)$	G^*	Q (0 to 18°C)
degrees C.									
0.03	$CH_3CO_2^-$	1	2	1.70×10^{-5}	4.469	55.0	1.439	0.160	12.7
	$CH_2OHCO_2^-$	1	2	1.36×10^{-4}	3.566	19.3	0.985	0.159	12.7
	$CH_3COCH_2CO_2^-$	1	2	2.57×10^{-4}	3.289	16.9	0.927	0.192	13.1
	H_2O	1	1	55.5	−1.74	0.00425	0.628–3	0.0315	12.7
17.94	$CH_3CO_2^-$	1	2	1.79×10^{-5}	4.447	232	2.065	0.694	
	$CH_2OHCO_2^-$	1	2	1.48×10^{-4}	3.528	81.4	1.610	0.702	
	$CH_3COCH_2CO_2^-$	1	2	2.62×10^{-4}	3.281	74.7	1.572	0.855	
	H_2O	1	1	55.5	−1.74	0.0180	0.255–2	0.133	

The "uncatalyzed" reaction may be explained as the result of the basic catalysis of water. If we neglect the effect of the association of the water molecules, $k_{H_2O} = k_0/55.5$, and the basic strength of water $K_{H_2O} = 55.5^{-1}$. In the experiments we have thus determined the catalytic constants of the four bases acetate, glycolate, and acetoacetate ions, and water.

In other reactions catalyzed by bases in general it has been found that the following formula holds approximately (see reference 4).

$$\frac{1}{q} k_B = G\left(\frac{p}{q} K_B^\circ\right)^\beta \tag{47}$$

Here K°_B is the basic strength of the catalyst at infinite dilution, p and q are statistical factors for the base, and β and G are constants characteristic of the reaction. In order to test the formula for the reaction here examined we plot $\log\left(\frac{1}{q}k_B^*\right)$ against $\log\left(\frac{p}{q}K_B^0\right)$ (see table 9 and figure 3). If we determine β from the catalysis of acetate and glycolate ions we get $\beta = 0.503$ at 0°C. and $\beta = 0.495$ at 18°C. Thus β is practically independent of the temperature. For the calculation of G from formula 47 we have used $\beta = 0.50$ (table 9). In figure 3 we have at both temperatures drawn straight lines with the slope 0.50 through the points for the acetate catalysis. The points for the acetoacetate catalysis fall a little above the lines, while those for the water catalysis fall a good deal below them. As seen from table 9 the catalysis of the acetoacetate ion is 20 per cent stronger than we find from formula 47 when we base the calculation on the acetate and glycolate ion catalysis. The water catalysis is only one-fifth of the calculated value. The deviation is in both cases practically independent of the temperature. Table 9 also gives the heat of activation Q in kilogram-calories calculated in the usual way. Q is practically the same for all the catalysts.

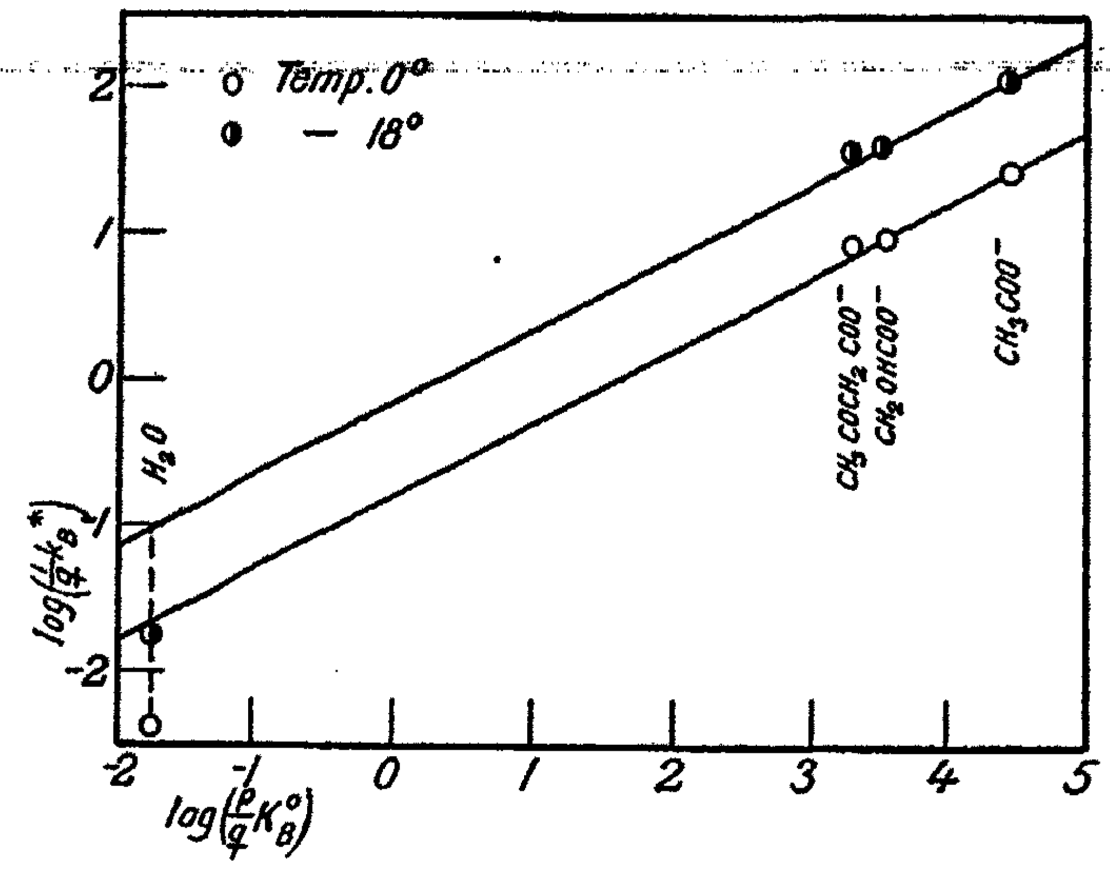

FIG. 3. BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ACID

VII. SUMMARY

The bromination of acetoacetic acid was studied in hydrochloric acid and in different buffer solutions. The experiments could always be explained from the assumption that the rate of bromination is determined by the enolization of the undissociated acetoacetic acid and α-monobromoacetoacetic acid, which reactions are catalyzed by bases in general, but not by acids.

The bromination was studied at 0°C. in hydrochloric acid of different concentration. The reaction follows scheme 1a-1d. From the experiments were calculated the unimolecular velocity constants for the enolization of acetoacetic and monobromoacetoacetic acids (the "uncatalyzed" or water reaction), and the dissociation constant of the latter acid.

The bromination of mixtures of acetoacetic acid and sodium acetoacetate was studied at 0 and 18°C. The gross reaction is expressed by scheme 7. The velocity is determined by the enolization of the undissociated acetoacetic acid. The velocity constant for the "uncatalyzed" reaction and the catalytic constant for the acetoacetate ion catalysis of the enolization were computed.

The bromination of acetoacetic acid in glycolate and acetate buffer solutions was studied at 0 and 18°C. The gross reaction is expressed by scheme 17. From the experiments were calculated the catalytic constants for the glycolate and acetate ion catalysis of the enolization of acetoacetic acid.

The dependence of catalytic constant upon basic strength was examined.

My thanks are due to Professor Niels Bjerrum for his kind interest in my work.

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THE INFLUENCE OF SALTS UPON INTERMITTENT PHOTOGRAPHIC EXPOSURES

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Received March 9, 1934

If, after an initial exposure sufficient to produce considerable developable density, a photographic emulsion is subjected to a second exposure to light of usually longer wave length, the existing density may be decreased. This is the Herschel effect.

Narbutt (10) has made a comprehensive study of the influence of various ions upon the Herschel effect. He concludes that the Herschel effect (with Satrox Universal Paper) is very strongly increased by the presence of Cu^{++}, Fe^{+++}, and VO^{++}. The remaining cations (of those investigated) have no marked effect. In the case of anions, F^- has little effect, Cl^- increased the Herschel effect considerably, and Br^- increased it very markedly. The anions CH_3COO^-, NO_3^-, and SO_4^{--} have no appreciable influence.

In general, both Narbutt and Trivelli (12) have found that the greater the decrease in sensitivity produced by a given ion, the correspondingly greater was the Herschel effect, and vice versa.

Perhaps during a photographic exposure two reactions exist, one a forward reaction making the silver halide grain developable, and the other a reverse reaction converting developable grains to their original state. The Herschel effect has been explained as the result of the preponderance of the reverse reaction. These and somewhat similar suggestions have already been reported (2, 3, 5, 6, 7, 8, 11). If we assume that a decrease in sensitivity is accompanied by an increase in the speed of the reverse *relative* to that of the forward reaction, the observations of Narbutt and Trivelli are explained.

Blair and Hylan (1) have suggested that the reactions (forward and reverse) which take place during exposure continue for a short time after the exposure has ceased. On this basis they were able to explain the findings of Davis (4) and others that intermittent exposures produce developable densities differing from those produced by equal continuous exposures. The reverse reaction, in the majority of cases, predominates over the forward during the periods of darkness between the intermittent exposures, and the resulting density is accordingly in these cases smaller than that produced by an equal continuous exposure.

TABLE 1

Developable densities produced by equal continuous and intermittent exposures upon treated paper

TREATMENT OF PAPER	EFFECTIVE TIME OF EXPOSURE	INTERMITTENT SECTOR OPENING	DENSITY BY CONTINUOUS EXPOSURE	DENSITY BY INTERMITTENT EXPOSURE	DENSITY RATIO
Unwashed	30	120°	1.53	1.445	1.06
	15	60°	1.29	0.80	1.61
	7.5	30°	0.54	0.21	2.52
Washed 1 hour	30	120°	1.52	1.50	1.02
	15	60°	1.52	1.47	1.04
	7.5	30°	1.36	1.06	1.29
	3.75	15°	0.64	0.375	1.71
Na_2SO_4 (1.5 per cent)	30	120°	1.50	1.46	1.02
	15	60°	1.37	1.09	1.26
	7.5	30°	0.745	0.39	1.91
K_2SO_4 (1.5 per cent)	30	120°	1.54	1.54	1.00
	15	60°	1.49	1.46	1.02
	7.5	30°	1.31	1.03	1.27
	3.75	15°	0.59	0.29	2.00
$NiSO_4$ (1.5 per cent)	30	120°	1.53	1.53	1.00
	15	60°	1.50	1.43	1.05
	7.5	30°	1.16	0.80	1.45
	3.75	15°	0.57	0.315	1.81
KF (1.5 per cent)	30	120°	1.56	1.55	1.02
	15	60°	1.52	1.47	1.03
	7.5	30°	1.345	1.03	1.31
	3.75	15°	0.61	0.415	1.47
KCl (1.5 per cent)	90	120°	1.50	1.37	1.10
	45	60°	1.29	0.74	1.74
	22.5	30°	0.50	0.19	2.59
KBr (1.5 per cent)	360	120°	1.49	1.46	1.02
	180	60°	1.46	1.32	1.11
	90	30°	1.37	1.01	1.36
	45	15°	1.15	0.54	2.11
	22.5	7.5°	0.80	0.23	3.52
$CuSO_4$ (1.3 per cent)	240	120°	1.52	1.53	1.00
	120	60°	1.50	1.40	1.07
	60	30°	1.26	0.71	1.77
	30	15°	0.56	0.15	3.71

TABLE 1—*Concluded*

TREATMENT OF PAPER	EFFECTIVE TIME OF EXPOSURE	INTERMITTENT SECTOR OPENING	DENSITY BY CONTINUOUS EXPOSURE	DENSITY BY INTERMITTENT EXPOSURE	DENSITY RATIO
Ferric ammonium sulfate (0.6 per cent)	840	120°	1.47	1.295	1.13
	420	60°	1.40	1.13	1.24
	315	30°	1.32	0.84	1.58
Silver nitrate plus citric acid (1 per cent each)	10	120°	1.51	1.47	1.03
	5	60°	1.41	1.38	1.02
	20	120°	1.49	1.49	1.00
	10	60°	1.44	1.41	1.03
	10	120°	1.27	1.35	0.94
	5	30°	1.225	1.21	1.01
	5	60°	1.15	1.07	1.07
	2.5	30°	0.95	0.98	0.97
	2.5	60°	0.523	0.495	1.06
$(NH_4)_2SO_4$ (0.8 per cent)	30	120°	1.50	1.45	1.04
	15	60°	1.45	1.36	1.07
	7.5	30°	1.23	0.99	1.24
Lead acetate (1.2 per cent)	30	120°	1.56	1.56	1.00
	15	60°	1.51	1.45	1.04
	7.5	30°	1.10	0.79	1.39
	30	30°	1.55	1.52	1.02
	15	15°	1.48	1.375	1.08
	7.5	7.5°	1.24	0.95	1.31
Sodium acetate (1.5 per cent)	15	60°	1.50	1.41	1.07
	7.5	30°	1.24	0.90	1.37
	3.75	15°	0.62	0.33	1.87
Ammonium chloride (1.5 per cent)	60	120°	1.37	1.365	1.01
	30	60°	1.21	0.80	1.52
	15	30°	0.47	0.24	1.95

The present paper deals with the influence upon the intermittency effect of many of the salts used by Narbutt, and in addition, certain other salts whose action upon the Herschel effect is known.

EXPERIMENTAL

A sensitized paper, Eastman Azo F No. 5, very strongly subject to intermittency effects, was used in this investigation. This paper was washed in gently running water for one hour to remove soluble salts. The paper was dried and immersed for ten minutes in various salt solutions and again dried. Each sheet was cut into two parts, one of which was given a series of intermittent exposures, and the other half a corresponding series of continuous exposures of the same total energy. Duplicate runs were made throughout.

The exposing light was diffused white radiation from an incandescent lamp. The intensity at the paper was 420 ergs per cm.^{2} per second. The intermittent exposures were obtained by means of a sector wheel placed directly in front of the emulsion. The apertures of this wheel were 120°, 60°, 30°, 15°, and 7.5°. The wheel was driven by a synchronous motor at the rate of 0.312 revolutions per second.

The exposed paper was developed for 90 seconds in elon-hydroquinone developer (D73), diluted one to three. The densities recorded are normal reflection densities.

Table 1 gives the results obtained with various salts at the dilutions specified. Each density value given is the mean of the duplicate runs except in the case of the silver nitrate–citric acid mixture. Owing to experimental difficulties in this case the individual variation was much greater than in the other determinations, and individual results of three runs are recorded.

DISCUSSION

In order to show more clearly the effect of salts upon intermittency, the data given in table 1 are plotted in figures 1 to 4. The densities produced by the continuous exposures are plotted as abscissae and the ratios of the densities produced by continuous and intermittent exposures as ordinates.

Figure 1 shows the result of washing upon the intermittency effect. The speed of the emulsion is increased (table 1) and the intermittency effect decreased. These differences are due primarily to the removal of soluble salts by washing, but they are probably partly due to the effect of water upon the emulsion itself.

Figure 2 indicates the method employed to isolate the effect of the individual ions (following the procedure of Narbutt in his study of the Herschel effect). Nickel sulfate, sodium sulfate, and potassium sulfate all produce practically no effect. Hence, it must be assumed that either the anions and cations have no effect separately, or that their effects are equal and opposite. The anions are the same in each case, while the cations differ considerably in properties. The assumption that these individual ions are without effect is accordingly the more plausible. This is further substantiated by the fact that sodium acetate is likewise without effect.

Figure 3 shows the effect of the halogen ions. The effect of I^- was to decrease the sensitivity to such an extent that data could not be obtained for paper treated with potassium iodide. The sequence here is the same as that found by Narbutt for their influence upon the Herschel effect.

A comparison of figures 3 and 4 will show that Cu^{++} increases intermit-

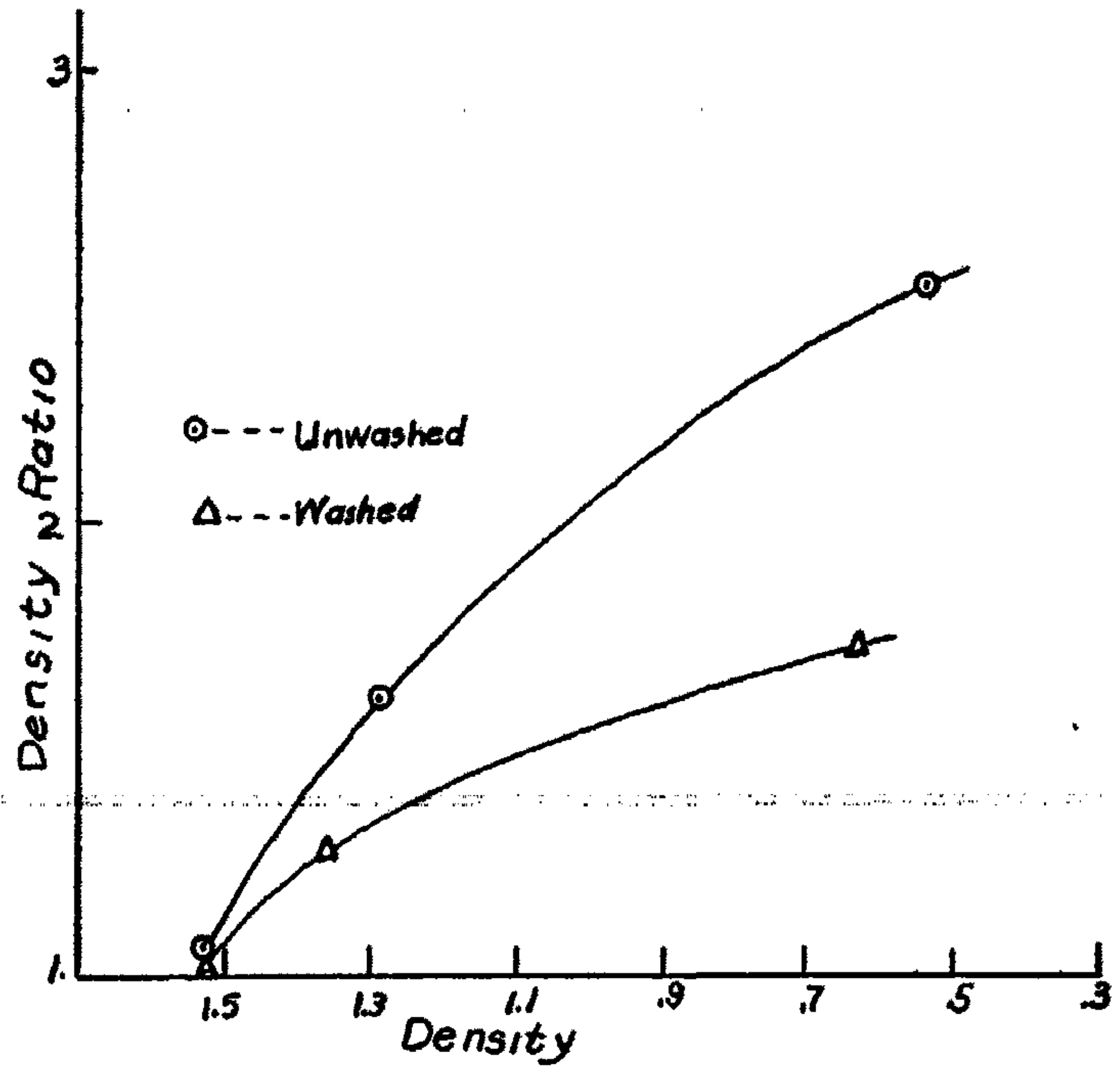

FIG. 1. THE INFLUENCE UPON THE INTERMITTENCY EFFECT OF WASHING THE EMULSION FREE OF SOLUBLE SALTS

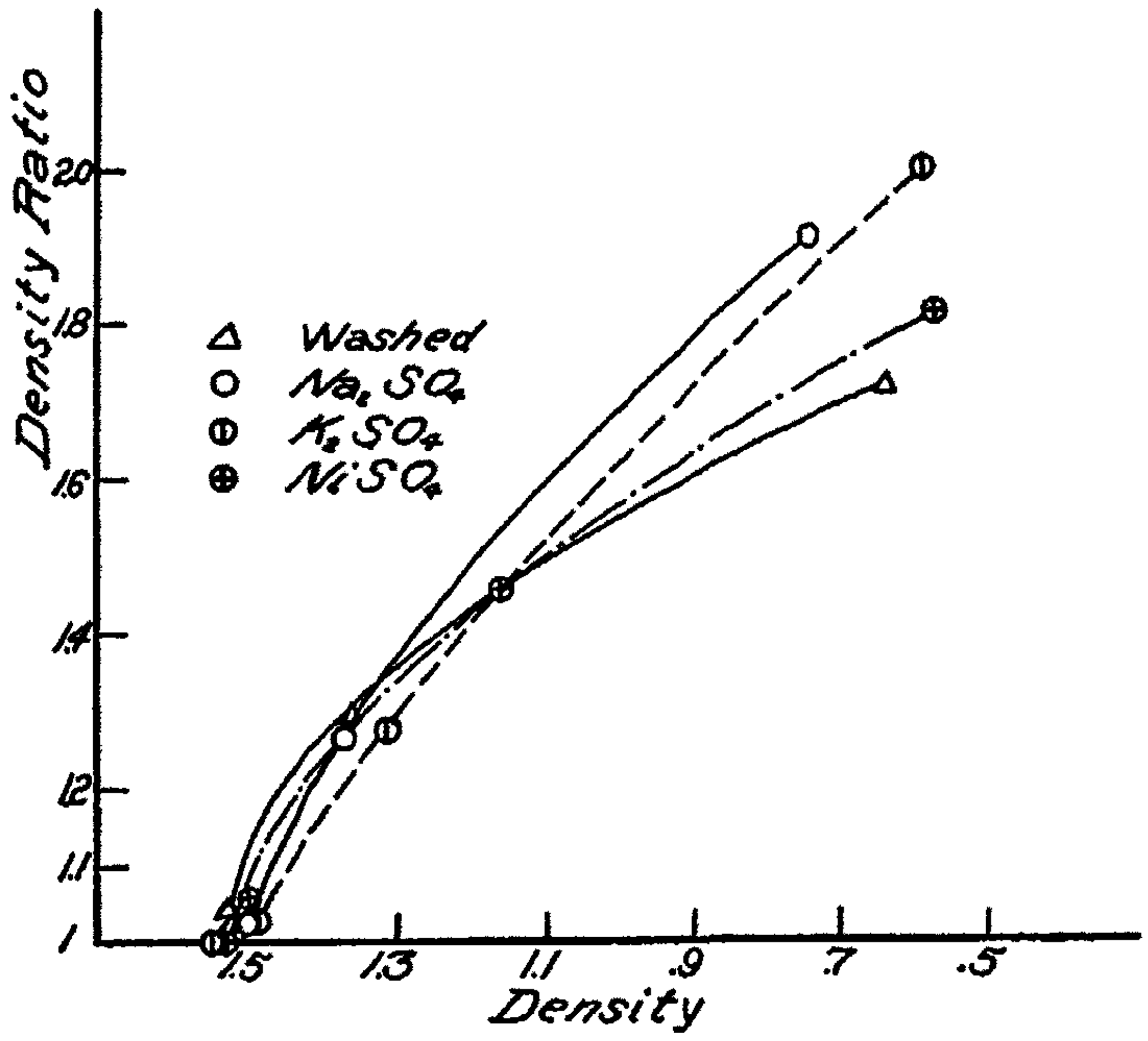

FIG. 2. THE ISOLATION OF THE IONIC EFFECTS INDICATING THAT Na^+, K^+, Ni^{++}, AND SO_4^{--} ARE NEUTRAL

tency effect almost as much as does Br^- for the concentrations used, whereas paper treated with a solution of 1 per cent silver nitrate and 1 per cent citric acid shows no intermittency effect. Lüppo-Cramer (9) has found that this solution prevents the Herschel effect, which again is in very good agreement with our initial thesis.

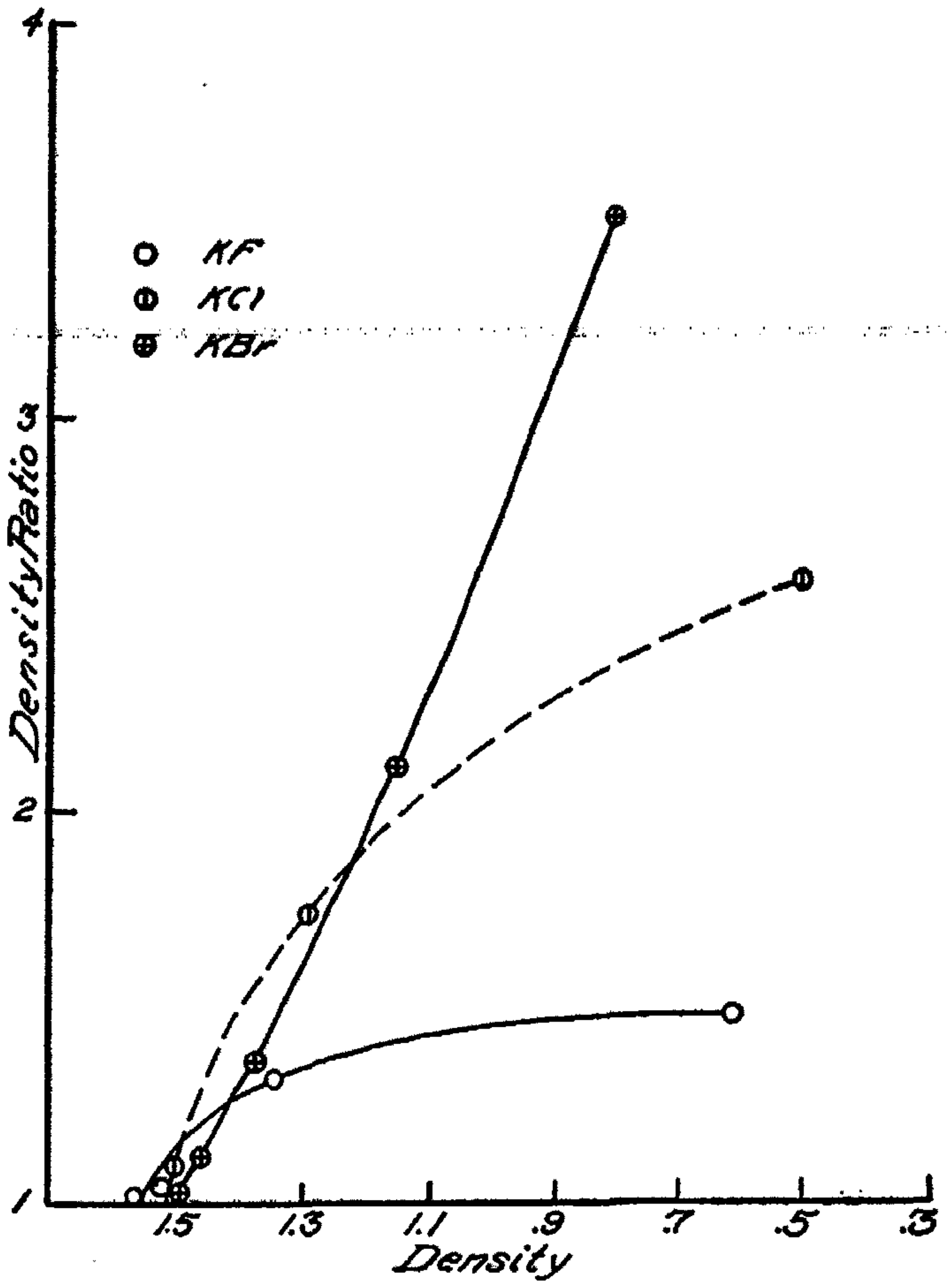

FIG. 3. THE ACTION OF THE HALIDE IONS UPON THE INTERMITTENCY EFFECT

The effects of the remaining ions were small. The ammonium ion apparently decreases the intermittency effect slightly, but a discoloration of the gelatin which invariably accompanied treatment with ammonium salts may, perhaps, make the results less reliable in this case. It is noteworthy, however, that these results are in agreement with those of Narbutt.

Pb^{++} likewise produced a small decrease in the intermittency effect, again in agreement with Narbutt. The remainder of the ions studied had practically zero effect.

In conclusion, it should be emphasized that not a single case was found in which the action of salts upon the Herschel effect, as reported by Narbutt, did not correspond to the action of the same salt upon the intermittency effect. Even the action of Ag^+, as found by Lüppo-Cramer upon a very different emulsion than the one we used (one very subject to Herschel effect, however), was the same. The general observations of Narbutt as to the relation which exists between the influence of an ion upon the

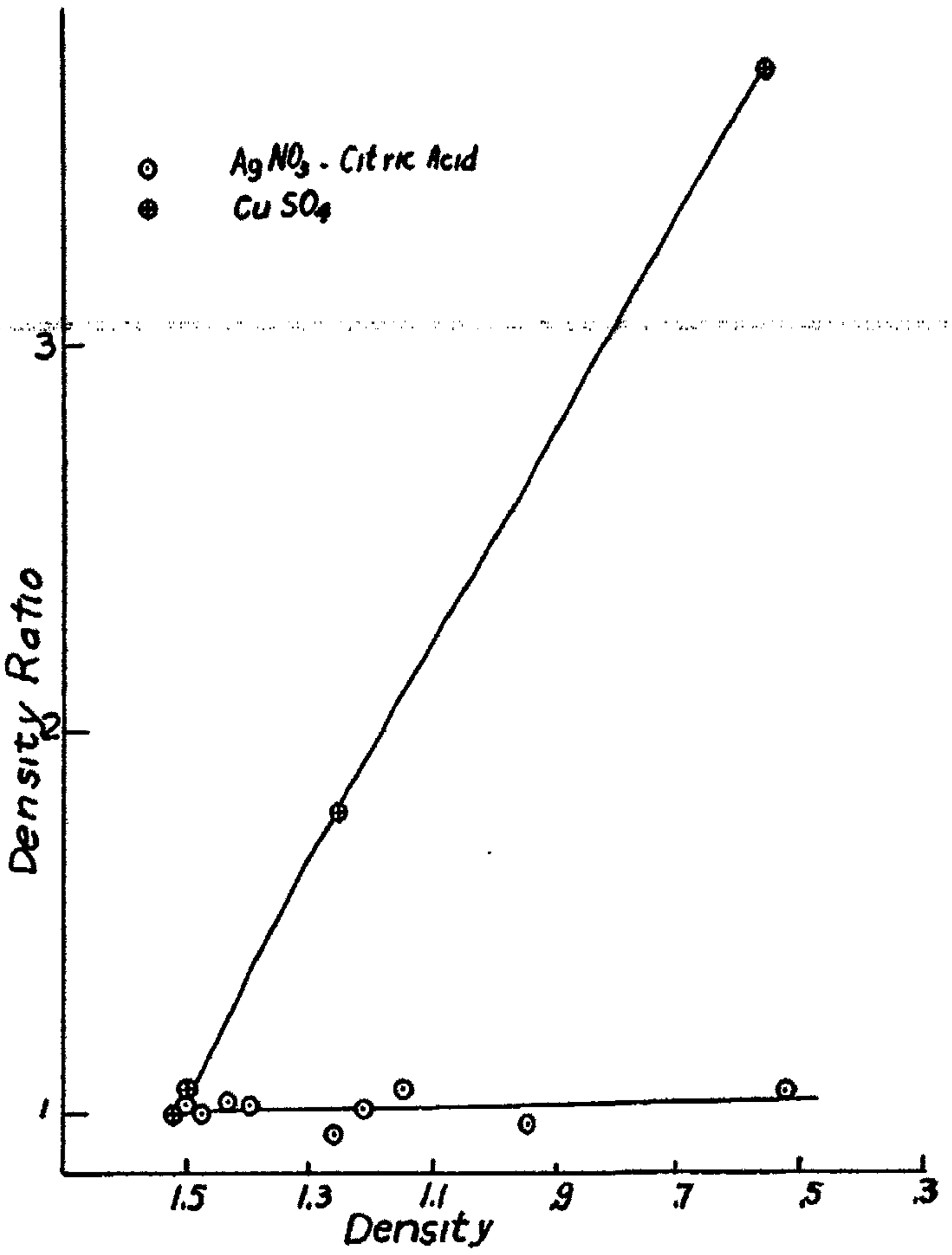

FIG. 4. THE ACTION OF Ag^+ AND Cu^{++} UPON THE INTERMITTENCY EFFECT

Herschel effect and its influence upon sensitivity of the emulsion evidently carries over to the intermittency effect. Accordingly, we feel safe in predicting that, in general, any salt which acts as a sensitizer or desensitizer for the Herschel effect will act in the same capacity for the intermittency effect.

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THE KINETICS OF THE REACTION BETWEEN GASEOUS METHYL ALCOHOL AND NITROUS OXIDE

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Received March 10, 1934

INTRODUCTION

In view of the progress that is being made in the study of the kinetics of gaseous oxidations by molecular oxygen, it is of interest to extend the field of investigation to include similar reactions in which oxygen is replaced by other gases.

Dixon and Higgins (1) measured the temperatures of spontaneous ignition of jets of different combustible gases in an atmosphere of nitrous oxide, and found that these temperatures were usually slightly lower—in the case of hydrogen considerably lower—than those obtained with oxygen. Since such experiments involve great uncertainty as to gas composition, they cannot yield definite kinetic conclusions, but they seem to indicate that the mechanisms of the two oxidation processes are similar.

In the case of the hydrogen-nitrous oxide reaction, Hinshelwood (4) concluded that the rate of the reaction was no greater than could be accounted for by the decomposition of nitrous oxide followed by rapid reaction of the oxygen and hydrogen. Melville (7) has recently carried out an extensive investigation of this reaction. His measurements showed that the reaction was from ninety to five hundred times as fast as the nitrous oxide decomposition, depending on the experimental conditions. The rate was directly proportional to the pressure of nitrous oxide and nearly independent of that of hydrogen, except when the nitrous oxide pressure was high. It was unaffected by nitrogen and argon. Increasing the diameter of the reaction vessel increased the velocity of the reaction. These facts are satisfactorily explained by a chain mechanism, and in this regard there is therefore a resemblance to the hydrogen-oxygen reaction.

It seems desirable to extend such investigations to other systems, and the present paper deals with the oxidation of methyl alcohol by nitrous oxide. The corresponding reaction with oxygen is of the chain type, and has been investigated fairly thoroughly by Fort and Hinshelwood (2).

APPARATUS

The reaction was followed in the usual way by observing the rate of change of pressure in a system of constant volume. The apparatus was similar to that used in previous investigations (3, 8). The gases were introduced in the desired proportions into a mixing bulb, and were then allowed to expand into the evacuated reaction vessel. Pressures were read on a capillary manometer, the dead space being about 2 per cent of the volume of the reaction bulb. The reaction vessel was a more or less spherical Pyrex bulb having a volume of about 200 cc. To prevent condensation of water vapor the capillary manometer and connecting tubing were kept at 65°C. by means of electrical heating. The reaction bulb was contained in an electric furnace, the temperature of which was kept constant to within 1°C. by the hand regulation of rheostats. Temperatures were measured by means of a chromel–alumel thermocouple.

The methyl alcohol used was obtained by the fractionation of commercial methanol, and distilled between 64.8°C. and 65.0°C. (uncorr.). Nitrous oxide was obtained in cylinders from the Ohio Chemical and Manufacturing Co., and was used without purification.

EXPERIMENTAL

Between runs the reaction vessel was evacuated for about one hour, the pressure being reduced to about 10^{-4} mm. As will appear later, all experiments were not strictly reproducible, but it was found that the time of pumping and degree of vacuum obtained had no effect on the rate of the following run.

DECOMPOSITION OF ALCOHOL

It is first of all necessary to show that the reaction under investigation is not the mere decomposition of methyl alcohol and of nitrous oxide. Blank experiments showed that even at the highest temperatures used the decomposition of nitrous oxide was barely detectable after thirty minutes. The rate of alcohol decomposition, however, was appreciable, occurring under various conditions of temperature and pressure at rates from one-fourth to one-twentieth of that of the main reaction. The rate of the alcohol decomposition was very sensitive to changes in the condition of the wall of the vessel. In general very low rates were obtained after the bulb had been used for several runs with nitrous oxide–methyl alcohol mixtures, and the rate increased progressively when a series of runs was made with alcohol alone. It would therefore be extremely difficult to make any accurate correction for the alcohol decomposition during the main reaction because of the variability of the rate of its decomposition, and also because its decomposition products might be oxidized. No correction has been made therefore, but the error thus introduced is probably not large. Some typical pressure-time curves for nitrous oxide-alcohol mixtures, and for alcohol alone are given in figure 1.

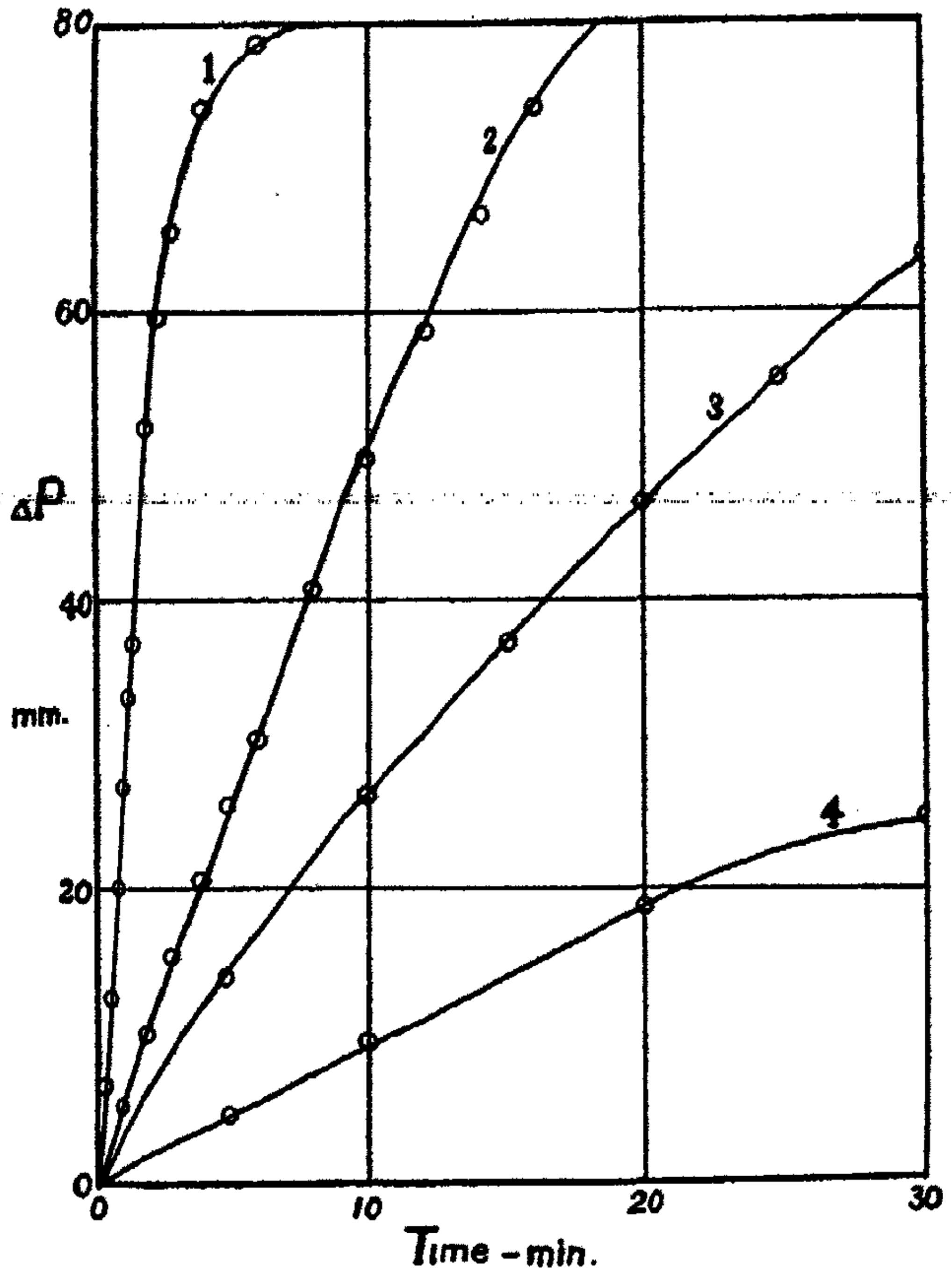

FIG. 1. TYPICAL TIME-PRESSURE CURVES AT 570°C.

Curve 1, 200 mm. nitrous oxide and 50 mm. methyl alcohol, packed bulb; curve 2, 200 mm. nitrous oxide and 50 mm. methyl alcohol, unpacked bulb; curve 3, 75 mm. methyl alcohol, packed bulb; curve 4, 75 mm. methyl alcohol, unpacked bulb.

THE PRESSURE CHANGE ACCOMPANYING THE REACTION

For the alcohol decomposition the average pressure increase when the reaction had reached completion was 126 per cent. In the case of nitrous oxide-alcohol mixtures the increase under all conditions was from 170 to 180 per cent of the initial partial pressure of alcohol. Had it not been for the accompanying decomposition of the alcohol the change would therefore have been about 200 per cent, provided that the decomposition products of the alcohol were not oxidized.

THE NITROUS OXIDE–METHYL ALCOHOL REACTION

Typical pressure–time curves are given in figure 1, and the data for a few typical runs in table 1.

The rates of reaction under various conditions have been compared by comparing the time required for a pressure increase equal to the initial alcohol content (t_{100}). The values of t_{100} for various mixtures at 570°C. are given in table 2. If these times are to be strictly comparable it is essential that the pressure–time curves should be of the same general form under all conditions, i.e., that the curves are affine. To test this, pressure–time curves for a number of runs chosen at random are plotted in figure 2. The time scales are varied so that some one point, other than the origin, is common to all of them. It will be seen that they coincide throughout their entire length.

TABLE 1

Data for typical runs at 570°C.

Ratio N_2O/CH_3OH	5:1	4:1	3:1	2:1	1.5:1
P_{CH_3OH} in mm........	48	51	56	48	52
Per cent pressure increase at completion relative to CH_3OH....	174	174	—	176	177
TIME	ΔP				
minutes	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*
0	0	0	0	0	0
1	4.8	5.6	4.8	2.9	3.0
2	11.8	11.8	9.4	6.5	5.6
3	18.0	17.6	14.2	8.7	9.0
4	23.6	23.6	19.2	12.5	12.8
5	30.0	28.8	22.4	16.3	16.0
6	35.8	33.6	28.2	19.7	19.2
7	41.2	38.6	—	—	—
8	46.6	43.2	37.2	26.1	26.0
9	51.4	47.6	—	—	—
10	56.6	51.6	45.4	32.7	32.0
12	64.6	59.6	54.4	38.7	38.2
14	74.2	65.8	62.2	44.9	44.0
16	80.6	71.8	69.6	49.9	49.4
18	82.8	77.2	75.8	54.7	54.4
20	83.4	81.6	81.4	59.1	59.0
25	83.6	88.6	—	69.7	67.8
30	83.6	88.6	—	75.1	75.2
35	83.6	88.6	—	82.7	85.0
40	—	—	—	84.3	89.2
50	—	—	—	84.3	92.0

REPRODUCIBILITY

The rates of reaction were not always strictly reproducible. This is undoubtedly due to the condition of the surface of the bulb. A very small amount of carbon was deposited during the reaction, and while the amount was unimportant in itself, it probably accounts for the variability of the surface. After a reaction bulb had been in use for some time there was no marked drift in the rate of reaction. Some of the earlier results with each reaction bulb have therefore been discarded.

TABLE 2

Values of t_{100} for various mixtures at 570°C.

N_2O/CH_3OH	p_{CH_3OH}	t_{100}	N_2O/CH_3OH	p_{CH_3OH}	t_{100}
	mm.	*minutes*		*mm.*	*minutes*
5	58.3	7.8	3	17.8	10.9
5	48.0	8.3	3	10.9	10.0
5	41.4	8.9	3	9.8	9.7
5	38.4	8.6	2	80.0	14.8
5	35.4	8.5	2	67.2	15.5
5	29.7	8.3	2	56.7	15.6
5	24.5	8.2	2	48.0	15.3
5	21.0	8.3	2	28.3	13.4
5	14.7	7.6	2	20.2	12.9
5	7.4	6.9	2	18.0	13.0
4	50.8	9.9	2	14.0	12.3
4	32.5	9.8	2	10.4	12.3
4	23.4	9.8	1.5	74.3	16.8
4	20.0	9.5	1.5	62.5	17.2
4	12.5	8.6	1.5	51.8	17.0
4	11.3	8.7	1.5	45.8	16.4
3	56.4	12.5	1.5	44.0	15.7
3	36.7	12.0	1.5	27.8	14.9
3	36.5	11.8	1.5	21.1	14.9
3	27.6	12.0	1.5	12.7	13.6
3	20.7	11.0	1.5	10.2	14.0

EFFECT OF COMPOSITION

In figure 3 the values of t_{100} are plotted against the initial partial pressures of alcohol for various nitrous oxide–methyl alcohol mixtures at 570°C. From these curves it is possible to construct a set of single reactant curves showing the effect of varying the pressure of one reactant while the other remains constant. This is done in figure 4. It will be seen that t_{100} is approximately inversely proportional to the concentration of nitrous oxide, and approximately proportional to that of alcohol. In other words, the rate can be approximately expressed by

$$\frac{-d(CH_3OH)}{dt} = K(N_2O)$$

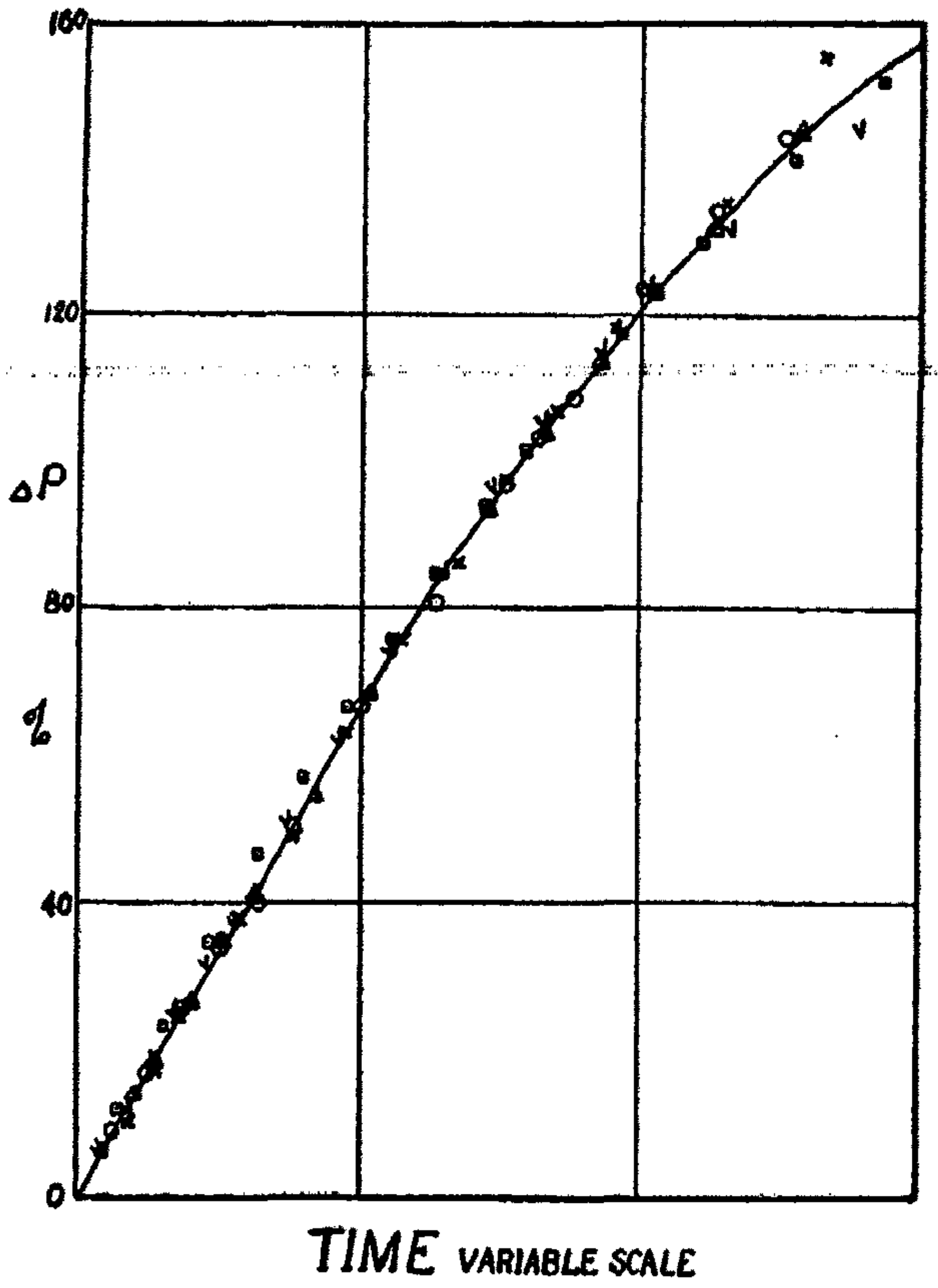

FIG. 2. AFFINE CURVES FOR VARIOUS NITROUS OXIDE-METHYL ALCOHOL MIXTURES AT 570°C.

TEMPERATURE COEFFICIENT AND EFFECT OF SURFACE

To determine the temperature coefficient of the reaction, a separate series of runs was made at different temperatures (in random order) with a mixture containing 50 mm. of alcohol and 200 mm. of nitrous oxide. Since the effect of packing the bulb on the rate of reaction is often the conclusive factor in determining the mechanism, a similar series was carried out with a reaction vessel packed with 1-inch lengths of Pyrex tubing. The surface was thus increased about six times, although the two surfaces are not necessarily strictly comparable on account of the deposition of carbon during the reaction. The results are given in table 3. It will be seen that the rate of reaction is roughly proportional to the area of surface. A series of runs showed that packing increased the rate of alcohol decomposition to almost exactly the same extent as it increased that of the main reaction.

In figure 5, log t_{100} is plotted against $1/T$. The apparent heat of the activation calculated from the slope of these lines is 59,500 calories per gram-molecule for the empty bulb, and 52,000 for the packed bulb.

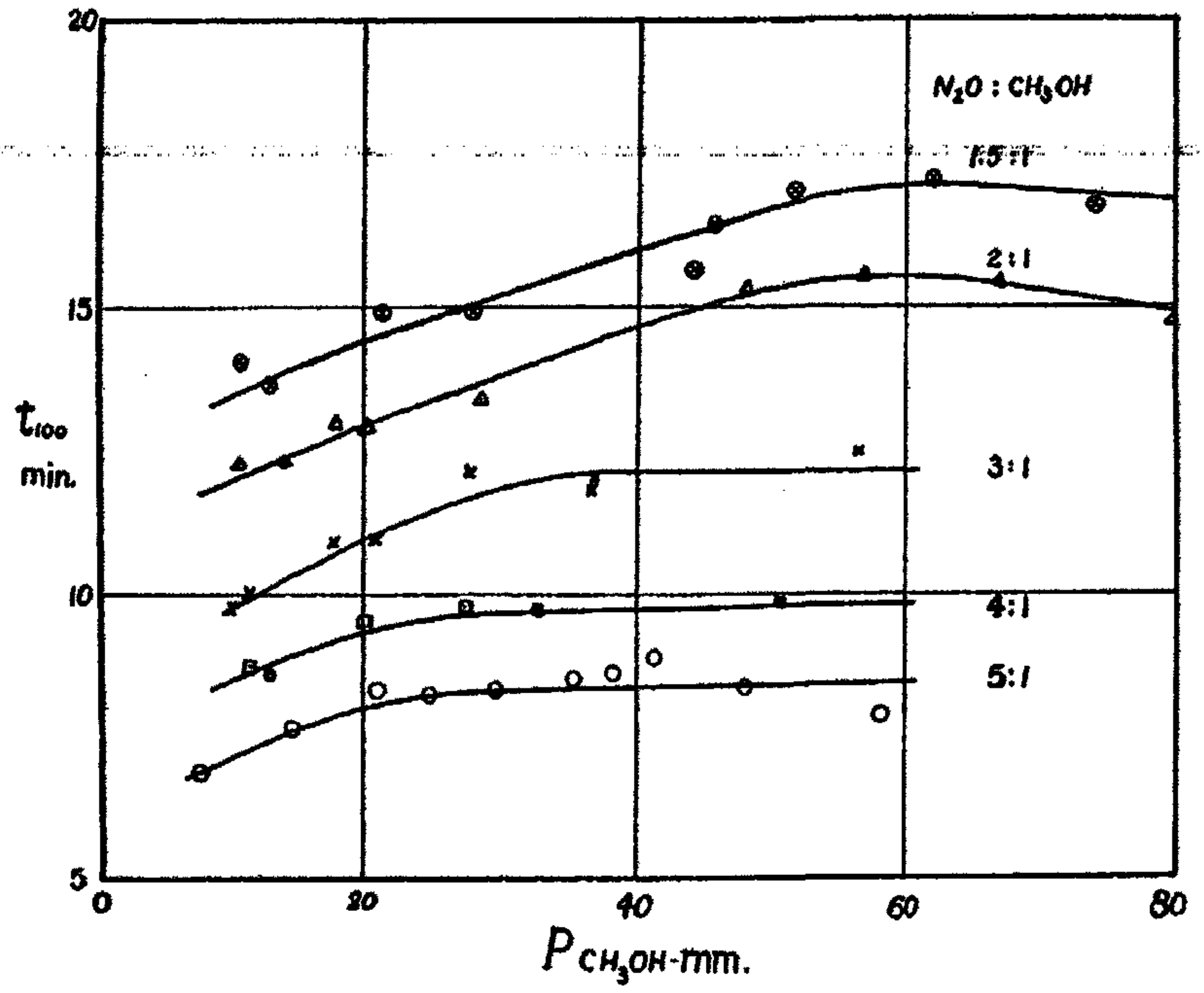

FIG. 3. THE EFFECT OF CONCENTRATION AT 570°C.

THE COURSE OF THE REACTION

The gaseous products analyzed were obtained mainly from runs made with the packed bulb at 570°C., and initial alcohol pressures of from 70 to 130 mm.

For the simple decomposition of methyl alcohol two analyses gave the following results: CO, 35.5, 33.8 per cent; CH_4, 2.0, 2.0 per cent; H_2, 61.5, 62.9 per cent. These results are in agreement with results given elsewhere (5) and indicate that the main reaction is

$$CH_3OH = CO + 2H_2$$

This, however, would require an expansion of 200 per cent, while that actually found was always about 126 per cent. It follows that a considerable amount of condensable products must be formed. Moreover, since the analysis shows a reasonably close balance between the constituents, the substances condensing out must have an empirical composition summing

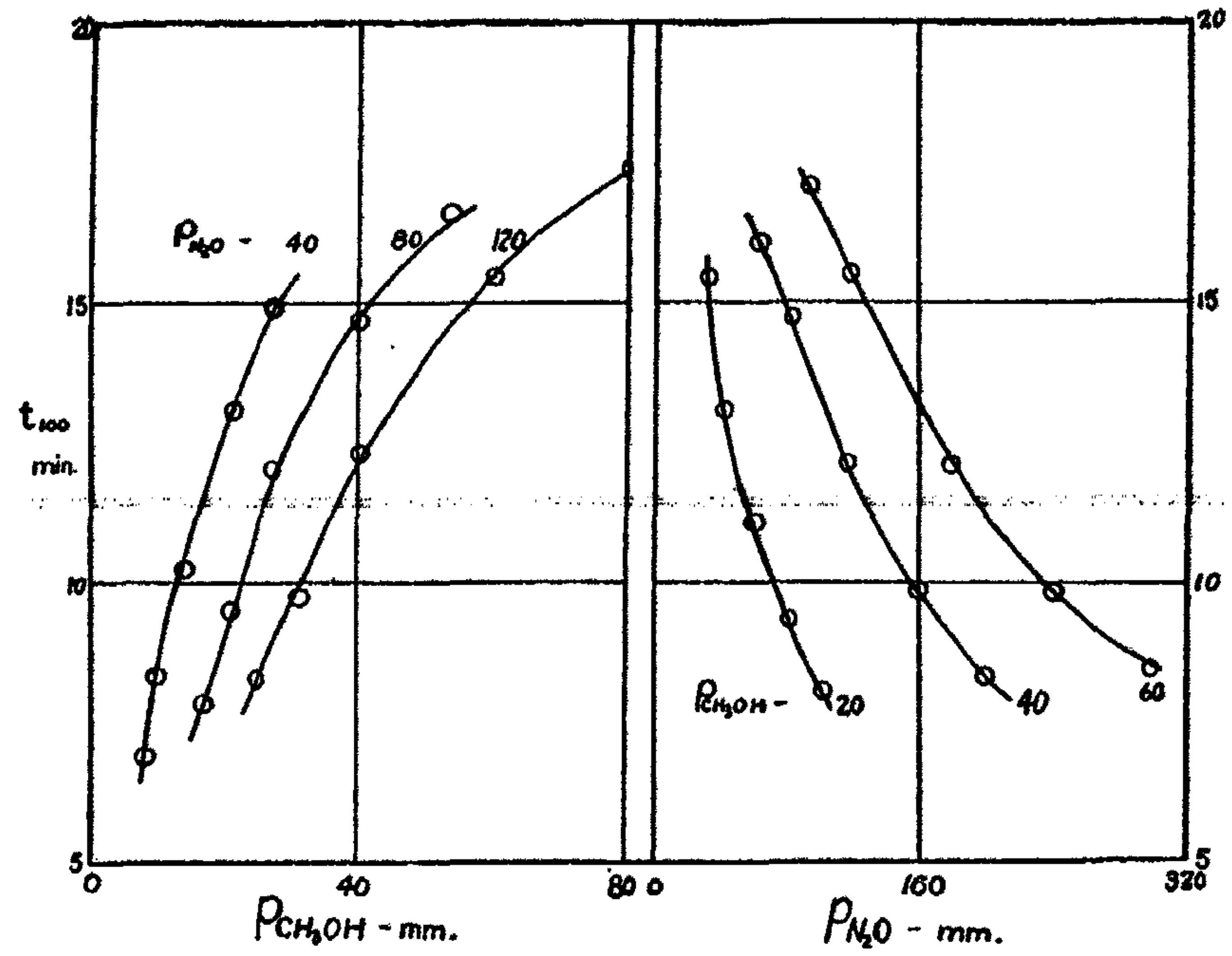

FIG. 4. THE EFFECT OF SINGLE REACTANTS AT 570°C.

TABLE 3

Temperature coefficient and effect of surface

TEMPERATURE	t_{100}		RATIO $\frac{\text{UNPACKED}}{\text{PACKED}}$
	Empty bulb	Packed bulb	
degrees C.	*minutes*	*minutes*	
500	162 195	26.1	6.8
520	90.8	9.1	10.1
535	48.5 49.0	6.8	7.2
550	22.4	4.3 4.7	5.0
570	9.3 10.2	1.83	5.4

up to approximately CH_4O. Since the alcohol decomposition is only a side reaction, it did not appear worth while investigating it further.

The analysis of the products of the nitrous oxide–alcohol reaction is complicated because of the solubility of nitrous oxide in all the customary absorbents (6). Inasmuch as the form of the reaction velocity curves is the same for all mixtures, the products of the reaction are almost certainly independent of the N_2O:CH_3OH ratio. Hence, in order to minimize the amount of nitrous oxide in the products, all analyses were made with a $1.5N_2O$ to $1CH_3OH$ mixture. The products thus obtained still contained some nitrous oxide. The solubility of this in potassium hydroxide and alkaline pyrogallol was not very serious, but fuming sulfuric acid and acid cuprous chloride dissolved so much nitrous oxide that they could not be

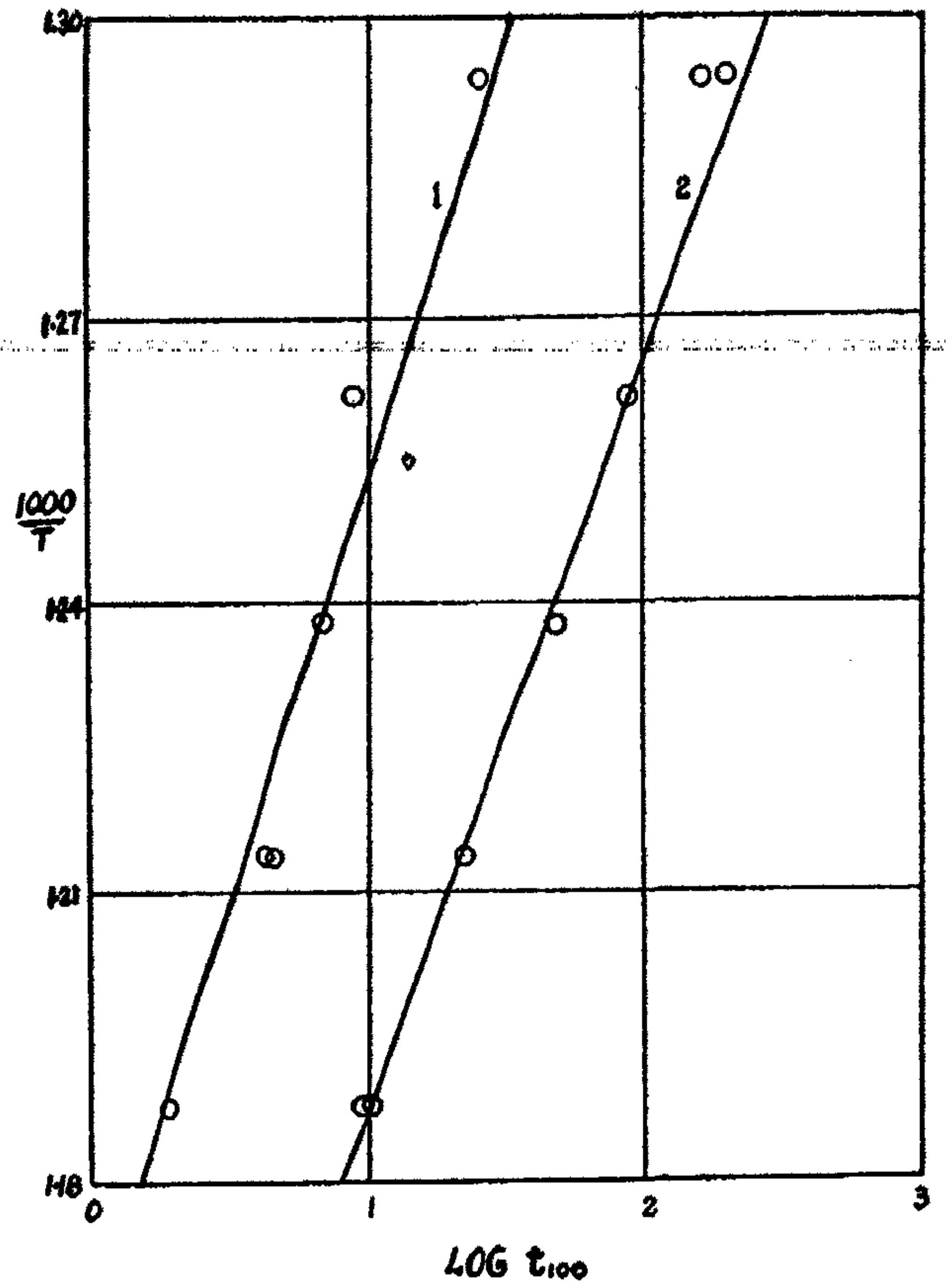

FIG. 5. TEMPERATURE COEFFICIENT

Curve 1, packed bulb; curve 2, unpacked bulb. $4N_2O + 1CH_3OH$. Total pressure, 250 mm.

used. For this reason the gas left after absorption of carbon dioxide and oxygen was transferred directly to the combustion pipet and burned with oxygen. On the reasonable assumption that the gas at this stage contained only carbon monoxide, hydrogen, nitrous oxide, and nitrogen, it is possible to determine the amounts of the individual constituents. In order to obtain a check, and especially to determine whether any nitrous oxide were lost in the two absorbents used, some samples were burned without previous treatment, and the carbon dioxide and nitrogen in the product determined. Three such determinations from runs at 570°C. gave: CO + CO_2, 23.6, 26.5, and 24.3 per cent, average 24.8 per cent; N_2 + N_2O, 45.9, 44.9, and 45.2 per cent, average 45.3 per cent.

Two analyses by the more complete method gave:

CO_2	O_2	CO	H_2	N_2O	N_2	CO_2 + CO	N_2 + N_2O
3.7	1.5	19.3	28.1	8.9	38.5	23.0	47.4
4.0	1.3	19.3	26.7	11.3	37.3	23.3	48.6

It will be seen that the values for CO + CO_2 and N_2 + N_2O are in satisfactory agreement with the values determined by direct combustion.

It is apparent that the ratio C:N is quite different from that which would be expected from the composition of the original mixture ($1.5N_2O$ + $1CH_3OH$). Thus if we use the values of nitrous oxide and nitrogen in the first analysis above to set up a material balance we have for the 94.8 parts of nitrogen,

	Carbon	*Hydrogen*	*Oxygen*
Calculated	31.6	126.4	79.0
Observed	23.0	56.2	38.6
Difference	8.6	70.2	40.4

The amount of carbon deposited in the reaction is far too little to account for the above. The missing hydrogen and oxygen are roughly in the proportions to form water. All three substances could be approximately accounted for by assuming H_2O + HCHO, but there was no evidence of an appreciable amount of formaldehyde, and in any case it is unlikely to be stable at such high temperatures.

If we use carbon as a basis for a balance, we have

	Nitrogen	*Hydrogen*	*Oxygen*
Calculated	69.0	92.0	57.5
Observed	94.8	56.2	38.6
Difference	25.8	35.8	18.9

Here the hydrogen and oxygen are almost exactly in the required proportions to form water. There is, however, a decided excess of nitrogen.

Suppose we assume that the primary reaction is

$$CH_3OH + N_2O = HCHO + H_2O + N_2$$

followed by

$$HCHO = H_2 + CO$$

and that we also have the side reactions

$$CH_3OH + N_2O = CO_2 + 2H_2 + N_2$$
$$2N_2O = 2N_2 + O_2$$

Then if we take $CO = 19.3$, $CO_2 = 3.7$, and $O_2 = 1.5$ as in the analysis, we have $H_2 = 26.7$, $N_2 = 26.0$, $H_2O = 19.3$, $N_2O = 8.5$. The actual analysis, averaging the H_2O on the basis of hydrogen and oxygen is $CO = 19.3$, $CO_2 = 3.7$, $O_2 = 1.5$, $H_2 = 28.1$, $H_2O = 18.4$, $N_2O = 8.9$, $N_2 = 38.5$. The agreement is very satisfactory, except for the excess N_2. It may therefore be concluded that the above scheme represents the general behavior, but that some condensation also occurs, the condensable material being oxidized in the process and hence liberating nitrogen.

There was no appreciable alteration in the products of reaction with changing temperature. Thus an analysis at 500°C. with a $1.5N_2O + 1CH_3OH$ mixture gave:

CO_2	O_2	CO	H_2	N_2O	N_2	$CO_2 + CO$	$N_2 + N_2O$
3.6	1.4	22.3	25.9	7.9	38.9	25.9	46.8

EXPLOSIONS

Attempts were made to obtain explosions in methyl alcohol–nitrous oxide mixtures at higher temperatures. In all cases there was merely a progressive increase in the reaction velocity with increasing temperature, without any sign of sharp limits.

DISCUSSION

The kinetic interpretation of the results is not without difficulty.

Since the rate of reaction is proportional to the surface area, it would appear at first sight that the reaction is of the ordinary heterogeneous type. If this is the case, then the approximate expression for the rate,

$$\frac{-d(CH_3OH)}{dt} = K(N_2O)$$

can be simply explained on the basis of fairly small adsorption of nitrous oxide. The heat of activation, however, is between 50,000 and 60,000 calories. This is somewhat larger than the value which would be expected for a homogeneous bimolecular reaction in the temperature region employed. It is consequently very high for a heterogeneous reaction. Moreover, if the reaction is a heterogeneous one, this is only the apparent heat of activation, and the true heat of activation must be higher than this. If the reaction were strongly retarded by the products or by one of the reactants, the apparent heat of activation might be higher than the true one. The results, however, give no indication of such an effect. It is, however, possible that variations in the relative adsorptions of the reactants may account for the high apparent heat of activation. The heat of activation found is approximately equal to that of the dissociation of nitrous oxide. This can have no significance, however, since the reaction is not homogeneous.

In the hydrogen-nitrous oxide reaction Melville found that the rate was approximately given by

$$\frac{-d(H_2)}{dt} = K(N_2O)$$

In this reaction the chains are initiated by the decomposition of nitrous oxide. It is therefore tempting to assume that the nitrous oxide-methyl alcohol reaction is also a chain reaction, in view of the formal similarity of the expression for the rate and of the exothermic character of the reaction. If this were the case, however, it would be necessary to assume that, unlike the hydrogen-nitrous oxide reaction, the chains are initiated at the wall and broken in the gas. The high heat of activation could be explained on the basis of a variable chain length, which makes the temperature coefficient a composite one. There is, however, no real evidence for a chain mechanism, and the fact that the reaction shows no explosive characteristics makes a chain process doubtful. It was mentioned at the outset that Dixon and Higgins obtained lower ignition temperatures in nitrous oxide than in oxygen for most substances. This would naturally lead to the conclusion that oxidations by nitrous oxide would occur at temperatures comparable with those at which the oxidations by oxygen take place. This, however, does not seem to be the case. In addition to the present investigation and that of Melville with hydrogen, it has also been found that ethylene and acetaldehyde (9) do not react appreciably until high temperatures are reached. It may therefore be concluded that nitrous oxide is only effective as an oxidizing agent at temperatures approaching those at which its decomposition becomes appreciable.

SUMMARY

The reaction between gaseous methyl alcohol and nitrous oxide has been investigated from 500 to 570°C. The rate is very much greater than that of the thermal decomposition of nitrous oxide. The rate of reaction is approximately proportional to the concentration of nitrous oxide and independent of that of alcohol. The apparent heat of activation is about 60,000 calories per gram-molecule. The rate of reaction is proportional to the surface area, and the reaction is therefore either heterogeneous, or a

chain process in which the chains are initiated at the wall. The main reaction is probably

$$CH_3OH + N_2O = HCHO + H_2O + N_2$$
$$HCHO = H_2 + CO$$

We wish to express our indebtedness to the National Research Council of Canada for a fellowship awarded to one of us (R. D. McD.) during the tenure of which this work was performed.

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NOTE ON THE OXIDATION OF CINNAMALDEHYDE

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Received March 16, 1934

The oxidation of benzaldehyde to benzoic acid is known to proceed through the stage of the peroxide, but the final result is the simple addition of oxygen to form the acid. The oxidation of cinnamaldehyde probably proceeds through similar intermediate stages; it is slower than that of benzaldehyde, and the final result is more than the simple addition of oxygen according to the equation,

$$C_6H_5CH{:}CH{\cdot}CHO + \tfrac{1}{2}O_2 = C_6H_5CH{:}CH{\cdot}COOH \qquad (1)$$

Much more than this amount of oxygen was used up by the cinnamaldehyde in the authors' experiments. Also carbon dioxide was formed as the oxidation proceeded, the rate of production of the carbon dioxide increasing with the time. Approximately 0.2 volume of carbon dioxide was formed while 1 volume of oxygen was absorbed; and 1 g. of cinnamaldehyde absorbed 220 cc. of oxygen, though oxidation was still uncompleted. (According to equation 1, 1 g. of cinnamaldehyde forms 1.12 g. of cinnamic acid and absorbs 85 cc. of oxygen; all gas volumes in this paper are at N.T.P.)

Moreover formic acid vapor was smelt—and confirmed—after the oxidation of some cinnamaldehyde in a closed vessel. The smell of benzaldehyde also was noticed at the end of similar oxidations. Among the oxidation products of a large amount of the cinnamaldehyde were found formic, benzoic, and acetic acids, which were roughly estimated: 100 parts of cinnamaldehyde gave 107 parts of cinnamic acid (maximum value), 0.7 part of benzoic acid, 4.5 parts of formic acid, and 0.4 part of acetic acid.

This work must be regarded only as preliminary work indicating that the oxidation of cinnamaldehyde proceeds in a complex manner. Experiments are needed on the oxidation of pure (100 per cent) cinnamaldehyde in pure oxygen, dry and moist, with and without removal of the carbon dioxide as it is formed, and in the presence or absence of the other products of the oxidation. It may be mentioned that benzaldehyde has been detected when cinnamaldehyde is oxidized by potassium permanganate (solutions), both by the authors and by Nicholls (3), and by others; that the accelerating effect of cinnamic acid on this oxidation is supported by the work of Almquist and Branch (1); and that acetic acid has been found in similar oxidations (2).

EXPERIMENTAL

The stock cinnamaldehyde, from Givaudan and Co., France, was colored yellow. The amount of cinnamic acid in this increased slowly from 4.5 to 7 per cent in three years. Some of the aldehyde was distilled in vacuo; after one such distillation the acid content was 2.0 per cent, and after a second distillation 0.85 per cent. All the acid figures quoted were found by titrations in alcoholic solution with carbonate-free caustic soda solution, using phenolphthalein, and the results were calculated as cinnamic acid.

Gasometric experiments

Cinnamaldehyde was dropped on to a filter paper placed at the closed end of a eudiometer, which had been filled previously with dry oxygen; the eudiometer was then inverted over mercury, some air being introduced in these operations. Then the volume of the gas was read during the following days and reduced to N.T.P. The first diminution of gas was rapid, but finality was long delayed. The volume of absorbed oxygen was greater than that calculated from equation 1. Also the titration of the final product indicated a quantity of acid which, assumed to be all cinnamic acid, should have resulted from a smaller volume of oxygen than that absorbed. Some typical experiments were as follows:

(1) The original aldehyde used (stock) = 0.1712 g. In this the acid content = 0.0099 g. Thus the net aldehyde = 0.1613 g. ≡ 13.7 cc. of oxygen, by equation 1. The original gas = 44.3 cc. (probably 80 per cent oxygen). The contraction equalled 14.2 cc. after 2 days, 18.7 cc. after 10 days, and 20.0 cc. after 19 days. The "contraction" may be low, owing to oxidation before the volume can be read at the start and to presence of carbon dioxide, here unmeasured. The acid formed by the oxidation, calculated as cinnamic acid, was 0.1513 g., which equals 11.5 cc. of oxygen (equation 1). In this experiment the oxygen was in excess.

(2) The original aldehyde (distilled) = 0.4241 g. In this the acid content = 0.0085 g. Thus the net aldehyde = 0.4156 g. ≡ 35.3 cc. of oxygen (equation 1). The original gas = 43.7 cc. The gas remaining was 11.9 cc. after 3 days, 12.2 cc. after 4 days, and 12.7 cc. after 7 days. The volume of 12.7 cc. consisted of 6.2 cc. of carbon dioxide and 6.5 cc. of nitrogen.

(3) An oxidation was carried out as above, except that samples of the gas were removed at intervals and were analyzed for oxygen and carbon dioxide. This experiment proved that the production of carbon dioxide

increased during the course of the oxidation. The first action is probably represented by equation 1, followed by side reactions.

(4) An experiment similar to experiment 2 was carried out with 0.355 g. of cinnamaldehyde spread over 0.2 g. of cinnamic acid in filter paper. This indicated a rather more rapid oxidation, reaching the same stage as the final stage of experiment 2 in 2 days. The presence of cinnamic acid therefore may accelerate the side reactions.

(5) An experiment similar to experiment 1 was carried out with benzaldehyde. The benzaldehyde used = 0.3734 g. In this the benzoic acid content = 0.0084 g. Thus the net benzaldehyde = 0.3650 g. ≡ 38.2 cc. of oxygen (equation 1). The contraction = 36.0 cc. after 1 day, and 36.1 cc. after 3 days. Titration of the final product indicated 0.3967 g. of benzoic acid, which corresponds to 36.4 cc. of oxygen. Benzaldehyde therefore oxidizes in the normal manner.

(6) In four experiments like experiment 2 the oxidation was started over mercury, and subsequently the carbon dioxide was removed by the introduction of caustic potash solution. The volumes of carbon dioxide produced per volume of oxygen absorbed were 0.166 (in 7 days, experiment 2), 0.198 (in 2 days, experiment 4), 0.213 and 0.225 (both in 6 days); mean value, 0.2. But this ratio of course will vary throughout the oxidation.

(7) This experiment was done with caustic potash solution over the mercury in the eudiometer throughout. The gas volumes were corrected for the vapor pressure of the caustic potash solution as well as for temperature and pressure; the temperature varied from 8°C. to 26°C., and the gas was kept, as usual, at about the atmospheric pressure, i.e., about 725 mm. The used cinnamaldehyde (distilled) = 0.2433 g. In this the acid content = 0.0019 g. Thus the net aldehyde = 0.2414 g. ≡ 20.5 cc. of oxygen. The gas volume was read over six months, and the following results are selected:

Time, in days	0	1	3	7	14	25	50	102	130	158	184
Contraction, or volume of gas absorbed, in cc.	0	18.5	24.7	31.9	36.9	41.5	44.4	47.9	49.6	50.65	51.4

The final ratio, $\frac{\text{Oxygen used}}{\text{Oxygen per equation 1}}$, is 2.51. In this experiment the oxygen was in excess throughout.

In a similar experiment the last ratio was 2.69 (over 190 days). This oxidation was probably completed; the final product had no smell of cinnamaldehyde, but it had a distinct smell of benzaldehyde.

(8) Similar gasometric blank experiments with the filter paper, in the presence or absence of cinnamic acid, and in oxygen either dry or over

caustic potash solution, showed no diminution in the volume of gas, i.e., no oxidation, for at least eighty days.

A large-scale oxidation

Cinnamaldehyde was placed in an open weighing bottle in a large vessel which was filled with dry oxygen. This aldehyde had been separated from the stock sample as bisulfite compound, regenerated, and distilled in vacuo; but it had been kept for twelve months in a desiccator before this experiment was started.

The original aldehyde = 20.94 g. In this the acid content = 1.54 g. Thus the net aldehyde = 19.40 g. In oxygen the gain in weight after 18 days = 0.42 g.; after 28 days = 0.54 g.; after 52 days = 0.98 g. In air the gain in weight after 74 days = 1.13 g. The total possible gain in weight according to equation 1 is 2.35 g.; in the experiment the oxidation is therefore about half completed. Also the gain of 1.13 g. corresponds to 10.45 g. of cinnamic acid according to equation 1. The resulting acid crystals were separated from the liquid; the crystals weighed 8.7 g., and the liquid 13.4 g. As cinnamaldehyde saturated with cinnamic acid contains about 15 per cent of the latter, the liquid contains 2 g. of the acid, which therefore is the main product of the oxidation. The liquid was shaken with excess of caustic soda solution, and the emulsion was then shaken with ether. The aqueous layer was acidified, when 1.0 g. of aromatic acids was recovered; this product contained 5 per cent of benzoic acid, and the remainder was mostly cinnamic acid. The separated aqueous solution contained benzoic acid (0.01 g.), formic acid (0.4 g.), acetic acid (0.04 g.), and cinnamic acid (about 0.1 g. = saturated solution). The ethereal extract gave on distillation 8 g. of cinnamaldehyde and a higher boiling residue (aldehyde plus cinnamic acid plus any other products of oxidation and impurities). This residue was 1.3 g. Calling it cinnamic acid, the products accounted for were 11.1 g. of cinnamic acid, 0.06 g. of benzoic acid, 0.4 g. of formic acid, and 0.04 g.

TABLE 1

Changes in the physical constants of cinnamaldehyde on oxidation

PER CENT CINNAMIC ACID IN THE ALDEHYDE	DENSITY	VISCOSITY	DENSITY	REFRACTIVE INDEX
5.20	1.0492	0.0470	—	—
5.78	1.0506	0.0486	—	—
0.9	—	—	1.055	1.6217
7.0	—	—	1.064	1.6207
13.9	—	—	—	1.6179

of acetic acid, besides 8 g. of unchanged aldehyde; total = 19.6 g. The 22.1 g. of product thus would contain 9.1 g. of aldehyde, 12.5 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid. Allowing for the acid in the original aldehyde and for the unchanged aldehyde, it was found therefore that 10.3 g. of aldehyde (net) oxidized to 11.0 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid, besides the carbon dioxide found in the gasometric tests, and other probable products. There was found no oxalic acid among the oxidation products, and no formalin.

Benzoic acid was detected by the smell of ethyl benzoate and was estimated approximately by Nicholls' method (3). Acetic acid was detected by the smell of ethyl acetate and was estimated by distillation and titration and by afterwards checking the weight of the equivalent lead acetate. Formic acid was estimated by weighing the mercurous chloride reduced from mercuric chloride.

It was found that the crystals produced from the oxidation of cinnamaldehyde, although washed with benzene or carbon tetrachloride and subsequently dried for months in desiccators, only contained about 96 per cent cinnamic acid. Evidently small amounts of cinnamaldehyde become entangled and occluded in the crystals and final oxidation of these to acid is very slow. Melting-point determinations and a combustion analysis confirmed this supposition.

After titrating some oxidation crystals, which went 97 per cent cinnamic acid, the alcohol was distilled off, and the residue was extracted with ether. From the aqueous solution then the cinnamic acid was reprecipitated by adding hydrochloric acid; after washing well with water and drying in vacuo over sulfuric acid, the crystals analyzed 100.5 per cent cinnamic acid. Probably a trace of benzoic acid caused this high result.

As cinnamaldehyde oxidizes and holds more cinnamic acid in solution, the density and viscosity rise and the refractive index falls. Typical results are given in table 1.

The authors thank the Trustees of the Science and Industry Endowment Fund of Australia for a grant towards the expenses of the investigation.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XIV

THE IGNITION OF HYDROGEN-OXYGEN MIXTURES

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Received May 10, 1934

In previous papers (1, 2) the factors influencing the ignition of explosive mixtures of various gases in the condensed discharge were discussed in detail. The present communication describes a similar study of ignition in the positive column of the glow discharge. A $2H_2:O_2$ mixture was chosen for the study.

APPARATUS AND METHOD

The apparatus was the same as that described in the study of chain reactions in the positive column (3). In determining the conditions necessary for ignition, the discharge tube was first filled to the desired pressure, as read by a dibutyl phthalate manometer. The anode was lowered to exclude any positive column, and the discharge started at some low current. The anode was then raised until the desired length of positive column was introduced and the current was increased until ignition occurred, both the current and voltage being read at the instant of ignition. The fall of potential through the positive column was obtained by subtracting that for the negative glow from the potential drop between the electrodes.

RESULTS

The effect of pressure

The effect of pressure of the pure $2H_2:O_2$ mixture on the power input in the positive column for ignition is shown in table 1.

It will be observed that $(iV)\ P$ is constant to within the limits of experimental error. Thus the relationship between power input and pressure can be expressed in the form $(iV) = k/P$. This is in distinction to the condensed discharge, in which it was shown that $Q = k/P$, where Q is the quantity of electricity necessary for ignition.

The hyperbolic relation between power and pressure in the positive column is to be expected, from the fact that the heat developed as well as the number of active centers formed is proportional to the power expended.

In the condensed discharge, on the other hand, the spark jumps such a short distance that only part of the energy of the electron is dissipated in the gas; the production of active centers, therefore, is proportional to the number of electrons flowing rather than to the power.

TABLE 1

Effect of pressure of the mixture on the power input for ignition

P	$i \times 10^3$	V	$(iV)\,P$
mm. Hg	*amperes*	*volts*	
29.2	17.0	420	209
20.0	30.0	350	210
14.6	55.0	250	201

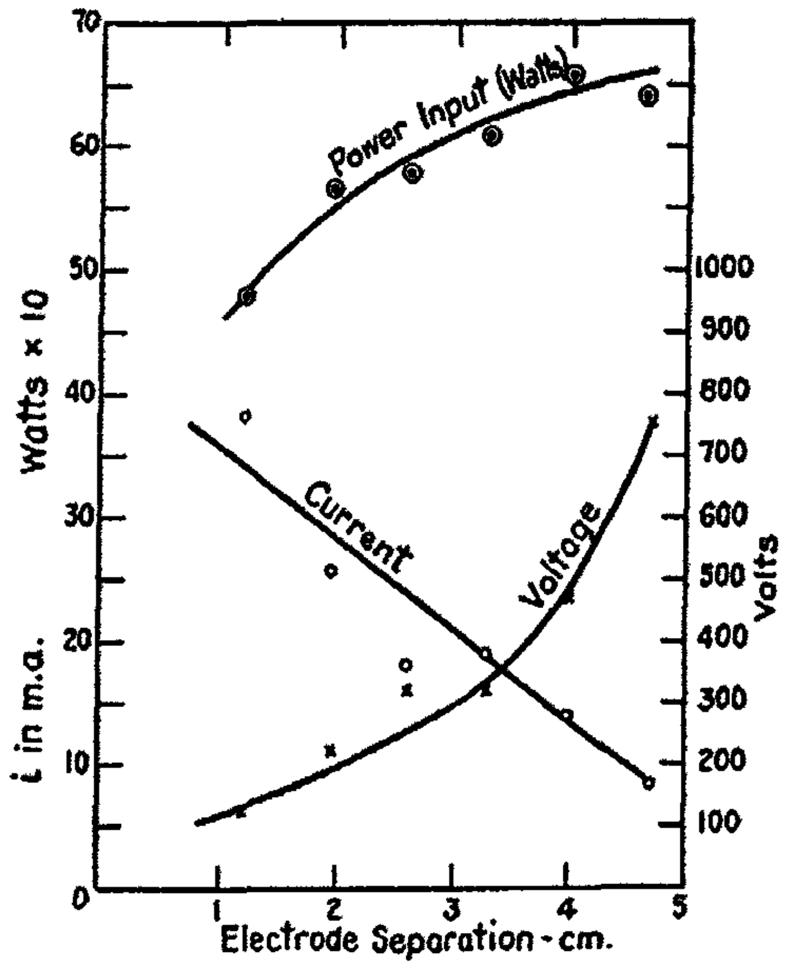

FIG. 1. THE EFFECT OF ELECTRODE SEPARATION

The effect of electrode separations

In figure 1 are given the current, potential drop through the positive column, and the power input at ignition for various separations.

It will be seen that while the ignition current decreases linearly with an increase in the electrode separation (d), the ignition voltage undergoes a rapid increase. The resultant power consumption increases only slowly with the length of the positive column, changing about 40 per cent for a threefold increase in electrode separation. The propagation wave was set up at some place in the positive column and not at either of the electrodes; in so far as could be told the electrodes themselves had no direct effect on the ignition.

The effect of the H_2:O_2 *ratio*

The effect of varying the hydrogen: oxygen ratio at constant pressure on the power input for ignition is shown in figure 2.

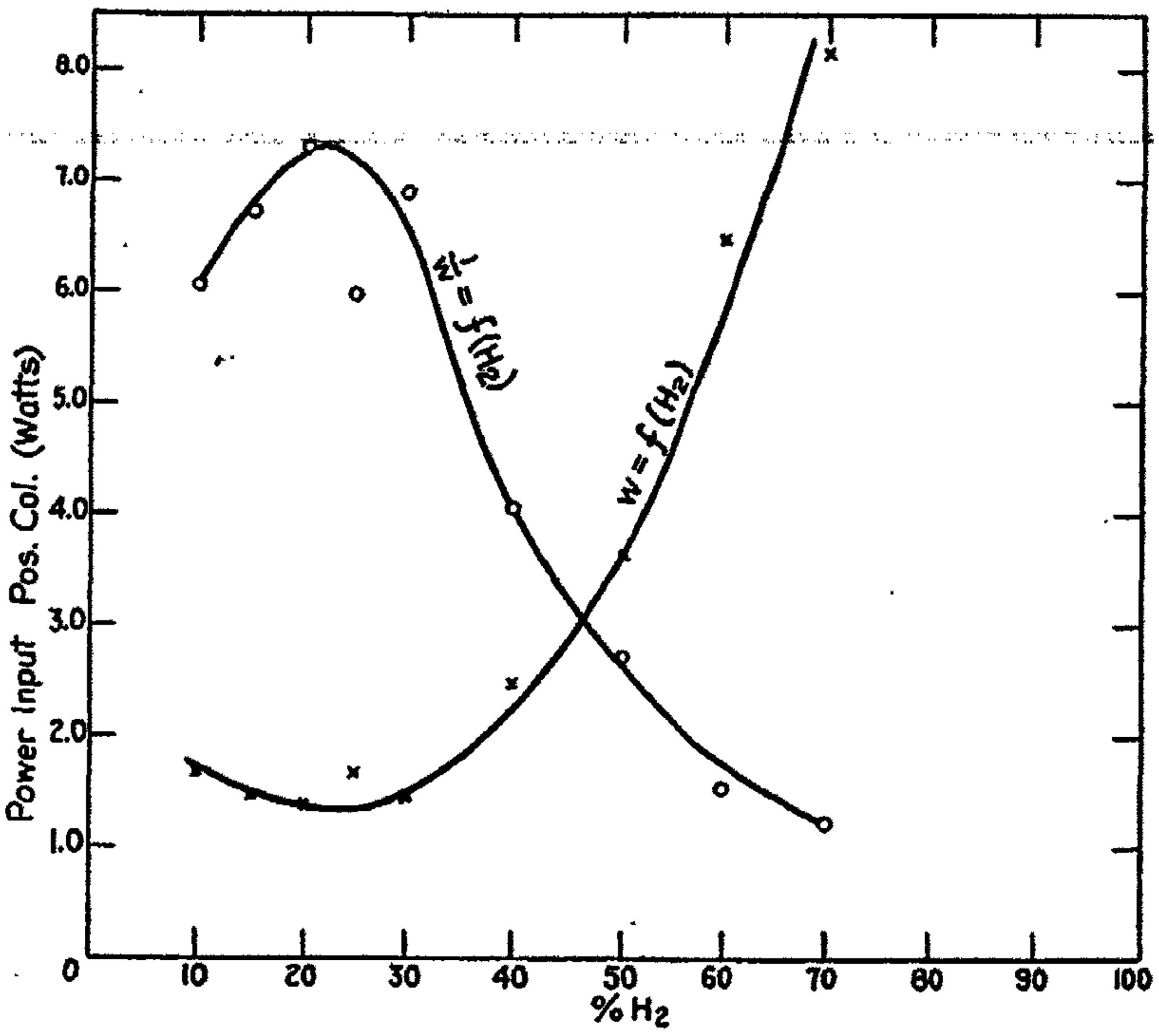

FIG. 2. THE EFFECT OF THE HYDROGEN-OXYGEN RATIO

The ignitability as given by $1/W$, and the power consumed, W, are both plotted. The power required for ignition reaches a minimum in a mixture containing 25 per cent hydrogen and 75 per cent oxygen; this power consumption is only 18 per cent of that required for the combining $2H_2$:O_2 mixture. This is in distinct contrast to the condensed discharge, in which excess oxygen had only a negligible effect on the quantity of electricity required for ignition.

The effect of added gases

The effect of various amounts of added gases on the power input for ignition is illustrated in figure 3. The partial pressure refers to the amount of gas added to 20 mm. of the $2H_2:O_2$ mixture.

The data show that the addition of hydrogen and helium to the explosive mixture results in an increase in the power for ignition, while water vapor, argon, nitrogen, oxygen, and nitrous oxide lower the explosive limit in the order named. The curves for oxygen and nitrous oxide were not symmetrical, owing primarily to changes they produced in the character of the positive column. Since the total pressure in the discharge was increased when the gas was added, the relative effects of these gases must be determined by a comparison with the $2H_2:O_2$ curve and not with the power input at 20 mm.

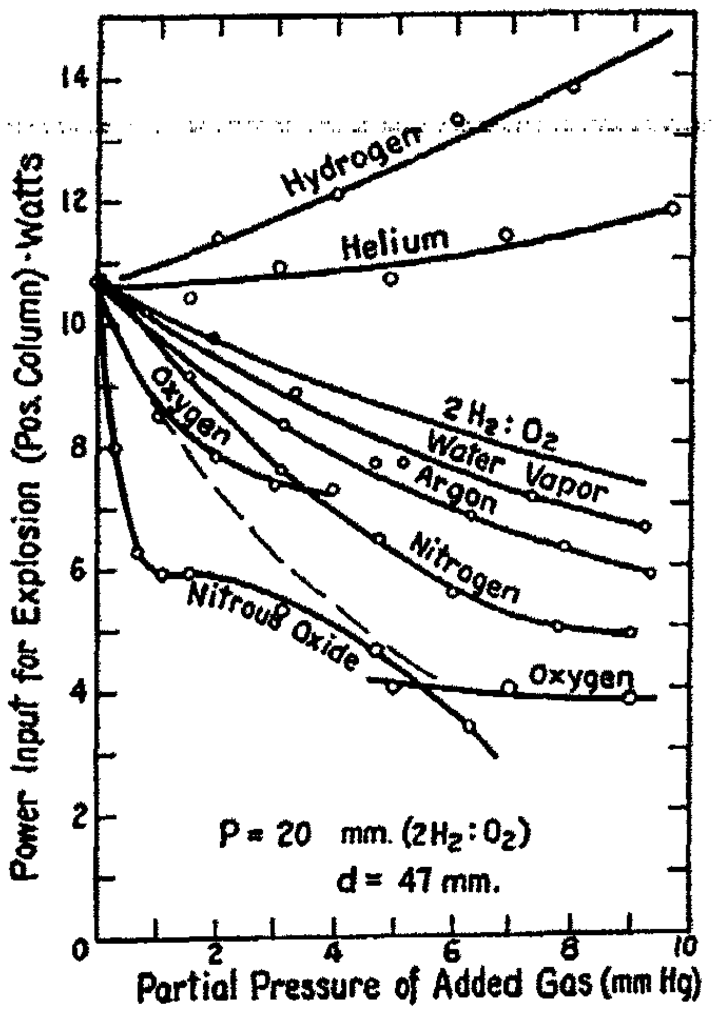

FIG. 3. THE EFFECT OF ADDED GASES

It will be observed that the order in which the various gases affect the ignitability is the same as that in which they affected the rate of reaction in the positive column for currents below that of ignition (3). The order is distinctly different from the effect of foreign gases on the rate in the negative glow (4). Likewise it is not at all the same as that found for ignition in the condensed discharge (2), where the order was more like that found in the negative glow, in that the ignition energy was lowered by hydrogen and raised by most other gases in accordance with the complexity of their molecules. The order is slightly different from that found by Hinshelwood and Gibson (5) for thermal ignition where the gases are placed $H_2O > A > N_2 > He$.

The effect of glass walls

The presence of surfaces in close proximity to the positive column increased markedly the power necessary for ignition, whereas such surfaces several centimeters removed from the path of the discharge had no effect. The power input for ignition was substantially the same in 1-, 3-, and 5-liter reaction chambers. In the case of a discharge between two aluminum rods 5 mm. long and 2 cm. apart, ignition occurred for the same power input when a glass cylinder 2.7 cm. long and 3.2 cm. in diameter was surrounding the discharge as when it was absent; the axis of the cylinder was placed perpendicular to the discharge. (In these tests the axis of the discharge was horizontal.) On the other hand, when the cylinder was replaced by a glass rectangle 1 cm. wide, 3.8 cm. long, and 3.2 cm. high, ignition could not be induced with the power available, which was over twice that used for the cylinder. When the cylinder was placed parallel to the direction of the positive column, the axis of both being vertical, the effect was much more pronounced; the gas could not be ignited with the available power input without adding excess oxygen to the explosive mixture.

The effect of the surface material was studied by surrounding the positive column with a concentric glass cylinder 1 in. long and 1½ in. in diameter, the cylinder being used both clear and heavily plated with silver on the inside. The diameter of this cylinder was sufficiently large to produce no effect on the power required to ignite the gas by a condensed discharge. The gas mixture chosen for the test was composed of one part of hydrogen and two parts of oxygen. The excess oxygen and the silver were chosen to test the effect of a possible production of ozone on the ease of ignition. The results showed that ignition occurred with 38 per cent smaller power input for silver than for the glass cylinder.

The effect of temperature

The ignition power input for various temperatures of the furnace surrounding the discharge tube is shown in figure 4.

These experiments were carried out at constant gas density, the pressure at room temperature being 20 cm. on the dibutyl phthalate manometer, which is equivalent to 1.54 cm. of mercury.

The data show that while the potential drop through the positive column increased somewhat with temperature, the actual power input for ignition decreased 8.75 times in raising the temperature from 300°K. to 600°K.

DISCUSSION OF RESULTS

The data just presented show that ignition in the positive column is distinctly different from that in the condensed discharge, in respect to the manner in which the ignitability is affected by the hydrogen:oxygen ratio, the presence of foreign gases, and the gas pressure. There is, however, a distinct analogy between the rate of reaction in the negative glow and ignition in the condensed discharge.

In the preceding article of this series a chain mechanism was developed which is adequate to account for the difference in reactivity in the positive column and in the negative glow (3). This mechanism involves two distinct steps in the ignition process: first, the production of active centers; and second, the setting up of reaction chains about these centers. The important consideration in this mechanism is that for propagation to occur the active center must be in a gas of energy density such that it can receive its energy of activation, E, by collision with the energy-rich molecules through which it is moving. This condition can be brought about by the influx of energy from the outside (electrical, thermal, etc.), or by the heat liberated in the primary reaction about the active centers initially formed in the discharge.

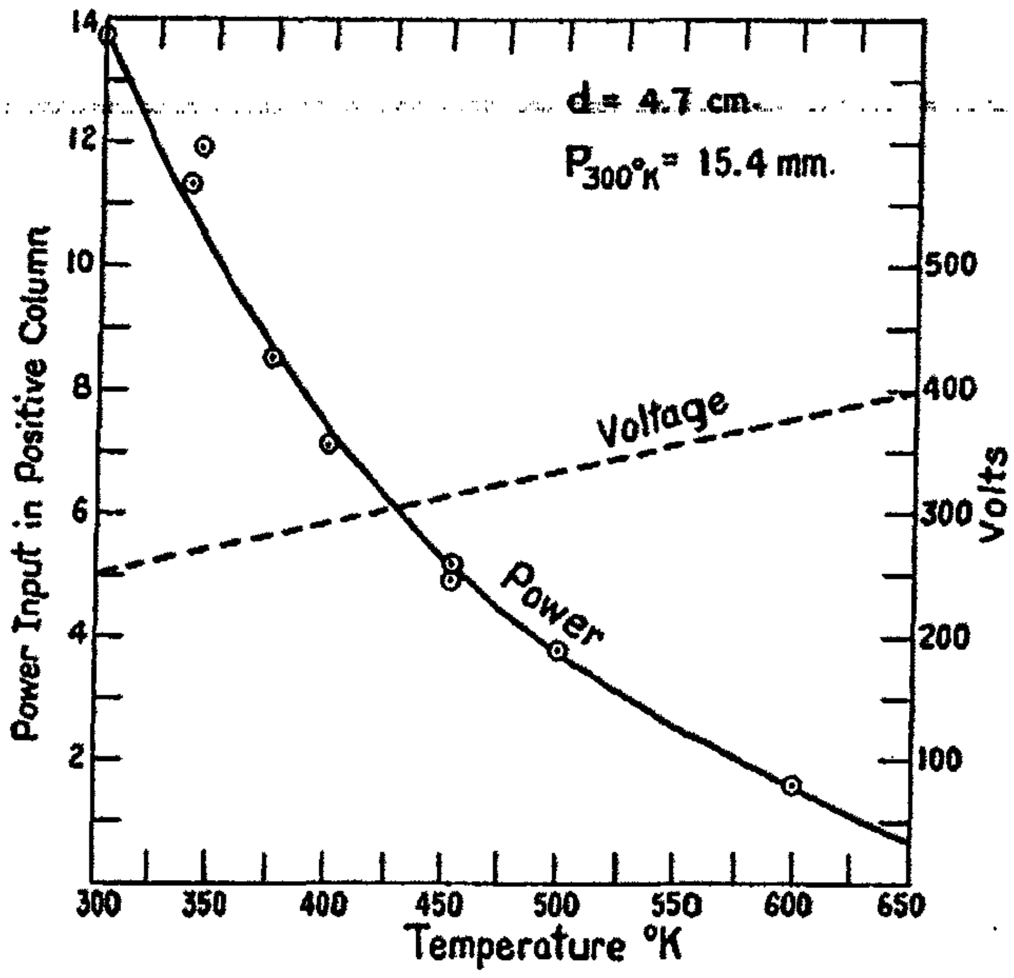

FIG. 4. THE EFFECT OF TEMPERATURE

This mechanism can now be used to account for the factors underlying ignition in the positive column, and for the differences found here and in the condensed discharge. Obviously ignition is dependent on the conditions which favor chain growth. In the case of the effect of added gases, as shown in figure 3, it will be seen that the various gases decrease the power input for ignition in the order of their respective abilities to retard the rate of diffusion out of the discharge. This determines the order in which these gases increase the energy density in the path of the discharge, and thus increase the chance of the active centers receiving the activation energy, *E*, by collision with energy-rich molecules. Flame propagation, a condition in which the heat of reaction is capable of supplying the necessary activation energy, starts somewhere in the space occupied by the positive column, and is encouraged, therefore, by any condition which raises the energy density of this region. The curves illustrated in figure 3 are in general segments of hyperbolas, as is to be expected from the data in table 1. From this it follows that the effect produced by the added gases is proportional to the number of molecules in the path of the discharge.

In the case of the condensed discharge (2) foreign gases raise the power input for ignition in order of their ability to absorb energy from the discharge, the order being almost directly opposite to that observed in the positive column. In this case the energy is all introduced at one time and in a very small volume. Since the gas molecules surrounding this volume are in the normal state, active centers diffusing out are lost. For flame propagation to occur it is necessary that a quantity of gas burn in the path of the spark sufficient to produce the energy-rich molecules that supply the energy *E* requisite for the continuance of reaction chains; the problem, therefore, is one of the production of a necessary number of reaction centers. In consequence, the presence of a foreign gas which absorbs energy from the spark decreases the number of active centers, and hence necessitates a higher power input to burn the amount of gas required for propagation. Since the rate of reaction in the negative glow is proportional to the rate of production of active centers, it follows from the above considerations that the order in which various gases affect the rate must be the same as that in which they affect the ignition in the condensed discharge. It should be mentioned that while added gases also absorb energy in the positive column, this effect is necessarily small compared to the gain from the reaction chains made possible by the retardations in the rate of diffusion.

The importance of the energy density of the gas surrounding the region through which the discharge passes can be obtained by comparing the difference in the ignition energy per unit volume for the positive column and for the condensed discharge. An exact estimation cannot be made, but the order of magnitude can be obtained as follows: Referring to figure 1 it will be seen that about 50 watts is required for an electrode separation of 1 cm.; under these conditions the positive column is about 10 mm. in diameter and 5 mm. long, with a volume of about 400 cu. mm. The power expended per cubic millimeter is 0.125 joule per second. In the condensed discharge at 1 cm. pressure, explosion occurs with 11 microfarads capacity at about 40 volts, the spark occupying not more than 1 cu. mm. of volume; the energy per cubic millimeter is 0.0098 joule. In the absence of inductance in the circuit the period of the discharge is between 10^{-4} and 10^{-5} seconds; this represents an expenditure of at least 98.0 joules per cubic millimeter per second. Since some energy is necessarily lost to the electrodes, a loss of as much as 50 per cent would still give an energy density four hundred times greater for the condensed discharge than for the positive column.

The effect of the energy density in the gas surrounding the discharge on the formation of reaction chains can be seen also from the various other factors influencing the ignition in the positive column. Thus, a twofold increase in the absolute temperature results in a ninefold decrease in the power input. Again, the power input per unit volume of positive column is decreased when the electrode separation is increased, as shown in figure 1. This would be very difficult to understand, since the ignition starts at localized points and not throughout the entire discharge at once, were it not for the fact that the energy flows from one segment of discharge into another, and thereby raises the energy density over that obtained from the power expended per unit volume alone; especially is this true in the present case where the axis of the discharge was vertical, so that the transfer of energy upward from lower portions of the discharge was aided by convection. The effect of surfaces near the discharge is also associated with the energy distribution. It is generally considered that reaction chains are broken upon contact with a surface. This, doubtless, accounts for the decrease in the reaction rate described in the previous communication (3), especially where propagation is possible. Walls surrounding the discharge break the chains, and, therefore, in limiting the reaction prevent the energy density from being raised to a point where ignition can take place. The fact that a silver surface lowers the ignition point less than does glass may be due to its ability to reflect the heat rays, thereby tending to raise the temperature of the gas in the path of the discharge.

SUMMARY

The factors influencing ignition in the positive column are contrasted with those obtained previously in the condensed discharge. Ignition does not occur in the negative glow, the N/H_2^+ ratio remaining almost constant irrespective of the pressure and power input.

The results show that the addition of foreign gases lowers the power input for ignition in accordance with the ability of these gases to retard the rate of diffusion; in the condensed discharge the order is almost the opposite, the work being increased in proportion to the amount of energy ab-

sorbed by the gas. The most easily ignited mixture of hydrogen and oxygen in the positive column is one containing 25 per cent hydrogen and 75 per cent oxygen.

A hyperbolic relation exists between power input for ignition and pressure.

The ignitability is increased ninefold for a twofold increase in temperature. It increases with the length of the positive column. It is decreased by the presence of surfaces near the discharge, but is unaffected by surfaces more than about 1 cm. removed.

The results are interpreted in the light of the cluster chain hypothesis presented in the preceding paper. The importance of the energy density of the gas surrounding the positive column is estimated by a comparison of the power input for ignition per unit volume of explosive mixture in the positive column and in the condensed discharge.

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PLATINUM ELECTRODE POTENTIALS IN MILDLY ALKALINE SUGAR SOLUTIONS, THE ELECTROMOTIVELY ACTIVE REDUCTANT PRESENT AND THE CATALYTIC EFFECT OF IRON ON ITS OXIDATION[1]

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Received June 18, 1934

It has long been recognized by those working in the field that platinum electrodes in alkaline sugar solutions do not acquire constant potentials which are so exactly reproducible as are observed on smooth electrodes in any of the reversible oxidation-reduction systems or on platinized platinum electrodes with hydrogen in the common buffers. Nevertheless, if conditions are carefully duplicated, the potentials are found to fall within a reasonably narrow range. They respond to the oxidation-reduction tendencies within the solutions. If a sufficient number of duplicate determinations be carried out, so that averages are significant, these electrode potentials can be made to yield considerable information concerning the complex equilibria existing in these solutions. This we have attempted to do and, in some thousands of experiments reported in this and previous papers (1, 3, 5), we have used more than a quarter of a ton of Merck's C.P. dextrose and a number of pounds of Bureau of Standards dextrose with which all findings were checked.

We shall consider first some of the reasons for the variability of platinum electrode potentials in sugar solutions at a pH not exceeding 10.5. Data will be given only for glucose. Other sugars, such as fructose, lactose, maltose, galactose, and sucrose, will, in general, yield qualitatively similar results. The cell, the potential of which was measured, was: platinum, sugar solution, saturated potassium chloride bridge, saturated calomel electrode. The temperature was kept at 30° ± 0.05°C. Unless otherwise stated, the apparatus and technic were the same as described in our previous paper (5).

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ADSORPTION EFFECTS

Clifton and Ort noted that for smooth platinum electrodes, which were in constant daily use and kept overnight in concentrated glucose solutions at pH 10, a simple rinsing with distilled water for the cleaning between runs resulted in the same potentials being registered by the electrodes as were observed following drastic treatment, such as standing in sulfuric and chromic acids, or in aqua regia, or heating to incandescence.

Tartar and McClain found that in certain solutions exposed to the air, smooth platinum electrodes had films adsorbed to them which extended a measurable distance out into the solution. Since many of our sugar solutions were made up exposed to the air, and since, even when air is carefully excluded, reducing sugars in alkaline solutions may attack the base or water to form oxygenated compounds, it was felt that adsorption of these oxygenated compounds of the sugars, or of oxygen itself, was the cause of the variability of platinum electrode potentials in these solutions.

A sugar solution was prepared, either by dissolving in the open air or by removing the oxygen from the buffer and electrode chamber with its dry sugar separately, by passing nitrogen through them for fifteen hours and then mixing them, precautions being taken to exclude the air at all stages of this process. When the electrode already in the chamber indicated the presence of a fairly strong reduction intensity, another similar electrode was heated to incandescence and, when cooled in the air for approximately fifteen seconds, so that it would no longer burn the finger if touched, it was plunged through a hole in the rubber stopper into the sugar solution, a particularly vigorous stream of nitrogen preventing entrance of any significant amount of air. The potential of this fresh electrode was then read at once and was invariably found to be considerably more reducing than the other electrode. However, the potential of the fresh electrode soon began to drift toward that of the other and, in time, both read approximately the same. For convenience, these electrodes will hereafter be designated respectively as "electrode No. 1" and "the fresh electrode." That these temporarily high negative potentials are not due to adsorption of any reducing gases from the flame during the heating to incandescence is shown by the potentials observed when the electrodes are plunged into a simple buffer solution which has previously been deoxidized. Here they always register, at first, a more positive potential than electrode No. 1, indicating that if any gas has been adsorbed it must have been oxygen.

A similar tendency of the fresh electrode to acquire more negative potentials than No. 1 electrode under these conditions was also noted in solutions of fructose, lactose, galactose, maltose, and sucrose, the difference between the potentials of the two electrodes being much less in solutions of fructose than in solutions of glucose and the other sugars studied.

Next, 0.1 cc. of a 30 per cent hydrogen peroxide solution was added to a solution of 60 g. of glucose + 100 cc. of a buffer, which produced a solution of pH 9.00. Before the peroxide was added, No. 1 read −0.387 volt, and a fresh electrode read −0.482 volt. Five minutes after adding the peroxide, No. 1 read +0.307 volt, and a fresh electrode +0.349 volt. Here the fresh electrode was the more positive. From these experiments the conclusion is almost inescapable that adsorption of something on the electrode is preventing in the one case a reductant, and in the other case an oxidant, from registering on the electrode the potential that their concentrations and positions on the scale of oxidation-reduction intensities should produce. However, if much greater excesses of either hydrogen peroxide or potassium ferricyanide be added, so that several hours must elapse before the oxidant is reduced, then the fresh electrode, at the instant it is introduced into the solution, will register a potential only a little less positive than that which No. 1 is showing and will rapidly drift toward the latter value. The presence of appreciable amounts of hydrogen or other fairly powerful reductants will also make the two kinds of electrodes register the same.

Thus, the adsorbed material which is preventing electrode No. 1 from acquiring potentials representative of the concentrations of reductant and oxidant existing throughout the body of the liquid, can be removed at least partially from the electrode either by reduction or oxidation. This may be a compound of oxygen and glucose which can be represented as GO, or, since the solution is alkaline, as GO^-. Its reduction may or may not yield the original glucose, but it does eliminate the strong tendency to adsorb on platinum.

Electrodes which had been for some time in equilibrium with mildly alkaline glucose solutions, were removed from the solution and waved for a few moments in the air. The still moist electrodes were then returned to the glucose solution and at once registered a more negative potential than they had before this removal. Apparently the oxygen of the air had reacted with the adsorbed compound and lowered its tendency to stick to the platinum. The adsorbed material, in view of these observations, could hardly have been oxygen itself. If such an electrode is rinsed well with distilled water and again introduced into the sugar solution, the potential becomes still more negative, approaching that of a freshly ignited electrode. We believe that in both these manipulations the adsorbed GO^- is converted at the surface of the platinum to GO_2^-, which is then easily removed, leaving a "clean" surface of metallic platinum which, for an instant, responds to the active reductant present in an unmodified manner. Adsorption of the GO^- ever present in these solutions at once begins and, with its greater local concentration of GO^-, gives a drift toward more positive potentials.

It has been previously noted (3) that under the proper conditions the addition of hydrogen peroxide to alkaline glucose solutions is followed by the formation therein of something intensely oxidizing. The oxidation potential goes up as high as +0.5 volt and more, which is more positive than can be observed with any concentration of pure hydrogen peroxide alone. We believe this high positive potential to be indicative of the presence of a glucose peroxide GO_2^-. Under these conditions the oxidation-reduction system, as far as the glucose is concerned, is $GO^- \rightleftarrows GO_2^-$. The coëxistence of any appreciable amounts of active reductant and GO_2^- would be impossible. The GO_2^- would be reduced by the active reductant almost the instant that the latter appears.

If oxygen be bubbled through such a solution at a rate to keep down the concentration of active reductant, small amounts of GO_2^- may be formed, at least momentarily, if another reductant is present which can be oxidized more easily by GO_2^- than by molecular oxygen. Shaffer and Harned have reported several such reactions and have assumed that in the oxidation of glucose there is formed first an oxide GO and then a peroxide GO_2, although they could get no direct evidence as to its existence.

It should be emphasized that these adsorption effects do not invalidate the determinations of the amount of active reductant present as carried out by Clifton and Ort. In those electrometric titrations the end point was determined by a jump in the peak potentials to more positive values, which indicated the momentary disappearance of all appreciable amounts of active reductant in the solutions. The actual potentials as read did not enter into the computation of the amount of reductant titrated. Neither does the adsorption interfere in the measurements of the rate of formation of the active reductant as carried out by Roepke and Ort, for, in making those measurements, large amounts of oxidant were added so that the solutions were kept strongly oxidizing for hours. Under these conditions, as mentioned before, we found no adsorption effects.

THE ELECTROMOTIVELY ACTIVE REDUCTANT

As stated in our former paper (5), we felt, because of the results of many other workers, that we had measured, in the case of glucose, the rate of formation of the 1, 2-enediol. However, as reactive as this form must be, it cannot exist long without undergoing chemical change. The electromotively active reductant, which accumulates even to the slight extent determined by Clifton and Ort, may not necessarily be this enediol form, through which stage the sugar may pass almost instantaneously.

An electrode was made by sealing a No. 18 platinum wire in the end of a glass tube and allowing it to protrude 1 mm. therefrom. Another electrode exactly like this was made, except that the exposed length of the wire was about 3.5 feet. Both were placed in the same electrode chamber in a solution of 60 g. of glucose +100 cc. buffer at pH 10.00, which was deoxidized by a stream of nitrogen. Both registered approximately the same reduction potential and, on titrating electrometrically according to the technic of Clifton and Ort, both gave the same end point at around 2.5 × 10^{-6} gram-equivalents of electromotively active reductant. Yet the exposed surface of platinum was one thousand times greater in the longer electrode.

Pin point electrodes, with the platinum surface polished off even with the fused end of the glass tube, gave somewhat more negative potentials; platinized platinum electrodes gave potentials that were still more negative. However, our standard No. 18 platinum wire electrodes of about 45 mm. in exposed length, such as we have used in all our recent work, when immersed in a solution with a platinized electrode in it, still registered the usual potential and gave the same titration end point, showing that contact with the platinized platinum electrode did not greatly modify the solution generally, once the solution reached equilibrium.

TABLE 1

Measurement of potentials

60 g. glucose; 100 cc. buffer at 30°C.

pH	PLATINIZED PLATINUM ELECTRODE POTENTIALS		SMOOTH PLATINUM ELECTRODE POTENTIALS	
	H_2 pressure 1 atmosphere	N_2 gas passed in at 1 atmosphere pressure	Momentary values	Acquired values
7.07	−0.425	−0.364	−0.340	−0.100
7.98	−0.480	−0.428	−0.415	−0.227
8.98	−0.540	−0.500	−0.481	−0.313
10.00	−0.601	−0.570	−0.529	−0.392

Table 1 shows the results of experiments done with platinized platinum electrodes and smooth platinum electrodes, such as we have already designated electrode No. 1 and fresh electrode.

Freshly prepared platinized electrodes were placed in glucose solutions just after the solutions had been made up in the open air, and nitrogen was passed in. The time necessary for these solutions to reach equilibrium in contact with the platinized electrodes is shorter than is required when smooth platinum electrodes are put into them. The potentials as registered became constant after several hours and reproducible to within 2 or 3 millivolts of the values indicated in the third column. When the nitrogen was then replaced by hydrogen, the ordinary hydrogen electrode potentials as recorded in the second column were obtained. Therefore, in the absence of any added hydrogen these electrodes, which readily reach equilibrium with molecular hydrogen, indicated potentials in these sugar solutions corresponding to hydrogen at 9.3 × 10^{-3} atmospheric pressure at pH 7, to 1.9×10^{-2} atmospheres at pH 8, to 4.7×10^{-2} atmospheres at pH 9, and 9.3×10^{-2} atmospheres at pH 10.

Other glucose solutions were prepared by deoxidizing the buffer and electrode chamber with the dry sugar in it separately with nitrogen for fifteen hours and then mixing out of contact with air. The potential on any platinum electrode in these solutions immediately after mixing is much lower than is found when this separate deoxidization is not done. After several hours, the comparatively steady potentials that No. 1 electrodes then registered were those recorded in the last column. These values can be duplicated with only rough approximation, since the time after solution is too short for the reducing sugar to reach completely the equilibrium that exists after from ten to fifteen hours. They are simply from selected individual experiments and must be compared with the simultaneous but momentary values of freshly ignited electrodes which are shown in the fourth column.

These fresh electrode potentials are usually reproducible to within 25 millivolts, or much less after the solution has stood for a somewhat longer time, or if the pH is around 9 and 10. They are "peak potentials," since the tendency of the electrode to reach equilibrium with the electromotively active reductant and to acquire a high negative potential is being opposed by the tendency of the electrode to adsorb GO^- and register a more positive potential. This latter process is more time-consuming, and hence, after a maximal reduction potential has been reached, a drift toward more positive values sets in. The platinized electrodes do not show this drift toward a more positive potential, but, if placed in the solutions soon after mixing and before the steady state is reached, they show a drift toward more negative potentials as the steady state is being set up. These platinized electrodes may catalyze at their surfaces some local reaction between the GO^- and the electromotively active reductant. Their potentials represent, then, maximal negative potentials which the peak values of the smooth fresh electrodes can never quite reach. These peak potentials correspond, in the case of pH 7 to 1.5×10^{-3} atmospheric pressure, of pH 8 to 6.9×10^{-3} atmospheres, of pH 9 to 1.1×10^{-2} atmospheres, and of pH 10 to 4.1×10^{-2} atmospheres of hydrogen.

We have emphasized the values for the partial pressures of hydrogen corresponding to these platinum electrode potentials because we feel that all the evidence is pointing to the conclusion that the electromotively active reductant accumulating to any appreciable extent in these sugar solutions, is actually molecular hydrogen. The partial pressures indicated are finite, although small. They correspond roughly in order of magnitude to the value of 2.5×10^{-6} equivalents of reductant for a solution similar to these at pH 10, as was determined by Clifton and Ort, and to a value of 1×10^{-5}, as has since been determined for pH 9 by the same technic. Data are not available for the solubility of hydrogen in solutions such as these. Approximately 1.5×10^{-4} gram-equivalents of hydrogen at atmospheric pressure will dissolve in 100 cc. of water at 30°C., which is about the amount of water in our solutions. Therefore, at pH 10 there should be $\frac{2.5 \times 10^{-6}}{1.5 \times 10^{-4}}$ or 1.67×10^{-2} atmospheres of hydrogen in solution. The platinized platinum electrode indicated 9.3×10^{-2} atmospheres, and the peak value of the fresh, smooth platinum electrode 4.1×10^{-3} atmospheres. Similarly, at pH 9 the 10^{-5} gram-equivalents of reductant corresponds to a pressure of 6.6×10^{-2} atmospheres. At this pH the platinized platinum electrode indicated 4.7×10^{-2} atmospheres, and the fresh, smooth electrode 1.1×10^{-2} atmospheres.

The addition of platinized asbestos to a solution of 60 g. of glucose + 100 cc. of buffer at pH 10 caused an instant shift in the potential of the smooth platinum electrode previously in the solution toward a more negative value. When about 10 g. of 5 per cent platinized asbestos was added to such a solution, the smooth platinum electrode in it acquired practically the same potential as a hydrogen electrode in a similar glucose solution at that pH but without any platinized asbestos. Small bubbles of hydrogen sometimes appeared in the arms of the salt bridge. P. M. Horton has also reported the evolution of hydrogen gas from alkaline glucose solutions in which finely divided platinum was suspended, and M. H. Power has noted a tendency of platinum electrodes in alkaline glucose solutions to approach the potential of a hydrogen electrode.

We believe that this finely divided platinum removes the GO^- from the solution by adsorbing it on its surface. GO^- as a factor in a chain of equilibria producing both GO^- and hydrogen being thus removed, more hydrogen can accumulate until equilibrium is again established. If enough platinized asbestos is present, this removal of GO^-, and the consequent disturbance of the equilibria, can continue to an extent sufficient to build up temporarily the hydrogen concentration equal to that supported by a pressure of 1 atmosphere of hydrogen. The addition of a considerable amount of potassium ferricyanide to such a suspension causes electrodes therein to become strongly positively charged. After a preliminary period during which accumulated reductants are oxidized, the remainder of the oxidant is reduced at approximately the normal rate, showing that the finely divided platinum does not markedly catalyze the rate of formation of the enediol.

When a similar concentrated solution of glucose at pH 10 is evacuated, a smooth platinum electrode previously placed therein may show but little change, probably because diffusion cannot remove hydrogen faster than it is formed. If, however, such an evacuated solution be shaken, or a small amount of nitrogen be allowed to bubble through the solution, expanding enormously thereby and violently agitating the solution, the electrode will, within a few minutes, become several tenths of a volt more positive. Similar shaking or the passage of a similar small amount of nitrogen through such a solution which is at atmospheric pressure, will produce comparatively little effect on the electrode potential. An extremely rapid stream of nitrogen at atmospheric pressure has been observed to change the electrode potential only about 7 millivolts. However, at pH 7 such a rapid stream passing through the solution at atmospheric pressure caused a shift in potential of 150 millivolts. Naturally the much smaller rate of formation will affect the net rate of removal by a gas in this manner. Similarly electrode potentials are more affected in this manner in dilute glucose than in concentrated solutions (4). These facts, taken together, show that a volatile reductant can be removed from these solutions by a vacuum or by the passage of a gas through the solution.

Finally if a solution of 60 g. of glucose + 100 cc. of a buffer to make the solution of pH 10 was placed in a 500 cc. distilling flask, which was then evacuated and sealed off from the vacuum pump, we found that after standing overnight, the gas which had collected over the solution could be pumped off by a liquid mercury pump and compressed into a small glass tube and measured. The amount of the gas thus collected, which was not water vapor, corresponded to a pressure of 1–2 thousandths of an atmosphere in the distilling flask. Pure oxygen was then admitted and mixed with this small amount of gas, and the mixture ignited by a glowing platinum wire. A contraction of one and one-half times the original volume of gas resulted. Confining the gas over a strong potassium hydroxide solution at any stage of the process did not change the results. We believe, then, that even mildly alkaline sugar solutions contain appreciable quantities of dissolved molecular hydrogen, which is in dynamic equilibrium with the sugars and their degradation products. It is the electromotively active reductant, the concentration of which is determined by the technic of Clifton and Ort.

OXIDATION AND ACCUMULATION OF HYDROGEN FOLLOWING THE ADDITION OF OXIDANTS

Clifton and Ort found that when oxygenated distilled water was added to glucose solutions at pH 10 in the absence of added iron, the peak potentials gave a curve similar to the solid line curve in figure 1. There was no end point. It seemed that the reaction, if any, between oxygen and the accumulated electromotively active reductant present was too slow, compared with the rate of formation of this reductant, to cause any sharp rise in potential when the amount of oxygen added just exceeded the amount of reductant present. This now seems reasonable, since molecular oxygen and hydrogen are rather inert toward one another.

When, however, a trace of iron was added, a curve, such as the solid line curve (figure 2) was obtained. We now believe that the iron catalyzed the reaction between oxygen and hydrogen under the conditions present in these solutions so that it sufficiently exceeded the speed with which hydrogen was formed, that any excess of oxygen present after all the hydrogen was destroyed would at once cause the electrode potentials to make a considerable jump toward more positive values. We believe that, in the presence of iron, oxygen can react rapidly with GO^- to form GO_2^-, and that the GO_2^- then rapidly oxidizes the hydrogen to form GO^- again and water.

Hence at pH 9 and 10 a detectable end point is possible, but not at 7 and 8 where the amount of accumulated hydrogen is too small.

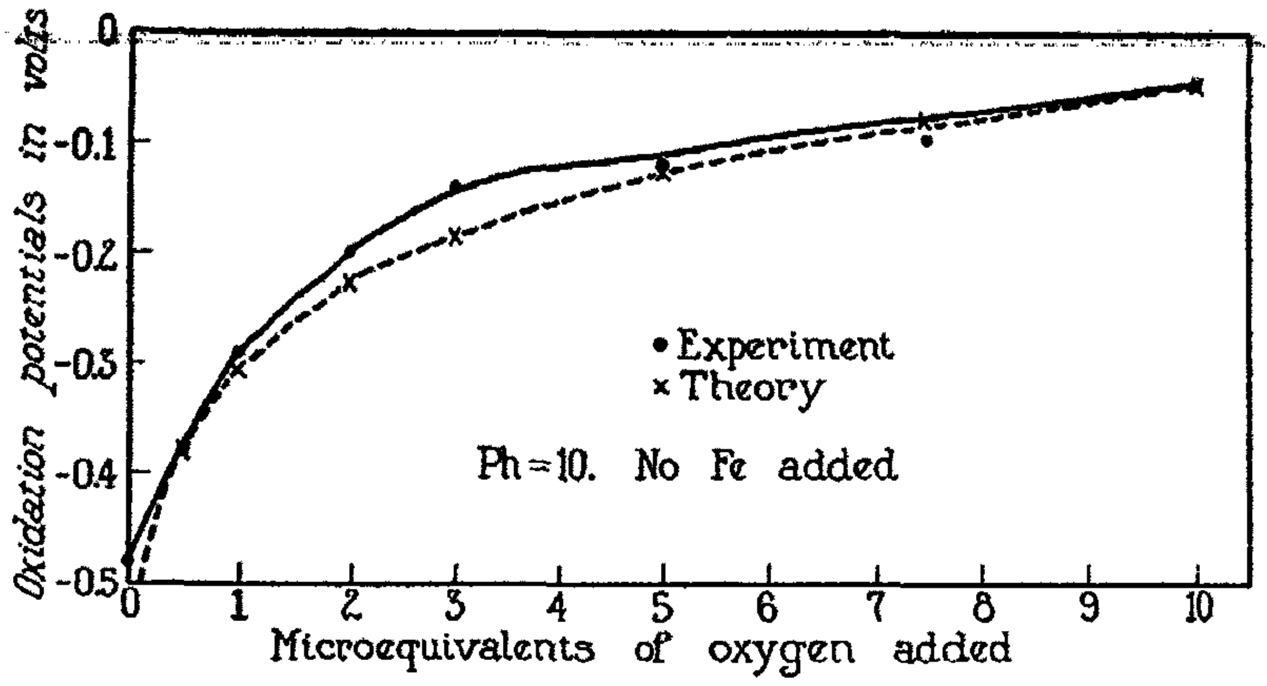

Fig. 1. Peak Potentials Following the Addition of Aerated Distilled Water

The time necessary to reach these peak potentials at pH 9 and 10 after the addition of the oxygen is never much longer than a few seconds, and often shorter depending on the amount of oxygen added. In fact, it could not be determined at all during a period of such rapid changing of the potentials, especially at pH 10, if it were not possible to set the potentiometer ahead of time approximately at the correct value as determined by previous trials. Very fast manipulation of the potentiometer is required then to determine the approximate peak potential, and the averages of many determinations were used to locate the points on our curves. We were aided somewhat by the fact that the most uncertain determination was the end point of our titration, which was just the point we were after. That is, for additions of lesser or greater amounts of oxygenated water, the voltage fluctuations near the peak voltages were much less in magnitude per unit of time. We also found it helpful to add the oxidant from a pipet carefully to the top of the sugar solution until the pipet was emptied, and then to mix suddenly by a violent agitation of the solution with an unusually strong stream of nitrogen gas and by shaking the electrode vessel by hand.

We may assume that, in the absence of added iron, neither the concentration of hydrogen nor the adsorption of GO^- at the surface of the electrode has been appreciably affected during this short interval of time. Their effects on the electrode potential would therefore remain constant. In this case the peak potential would be proportional to the logarithm of the concentration of the added oxidant. This proportional relationship to the logarithm of the concentration of added oxidant follows from the well-known Nernst formulation stating that oxidation potentials are proportional to the logarithm of the ratio of the concentrations of oxidant and reductant. Under these conditions the concentration of the reductant remains constant. When iron is present, and the indirect reaction between oxygen and hydrogen goes very fast, so that for the addition of only traces of oxygen there is an excess of hydrogen remaining and all the oxygen is gone, the potential should then be proportional to the logarithm of the amount of hydrogen in excess, since it is the only varying factor momentarily. When an excess of oxygen is added, and all the hydrogen is gone, the potential should be proportional to the logarithm of the amount of oxygen in excess.

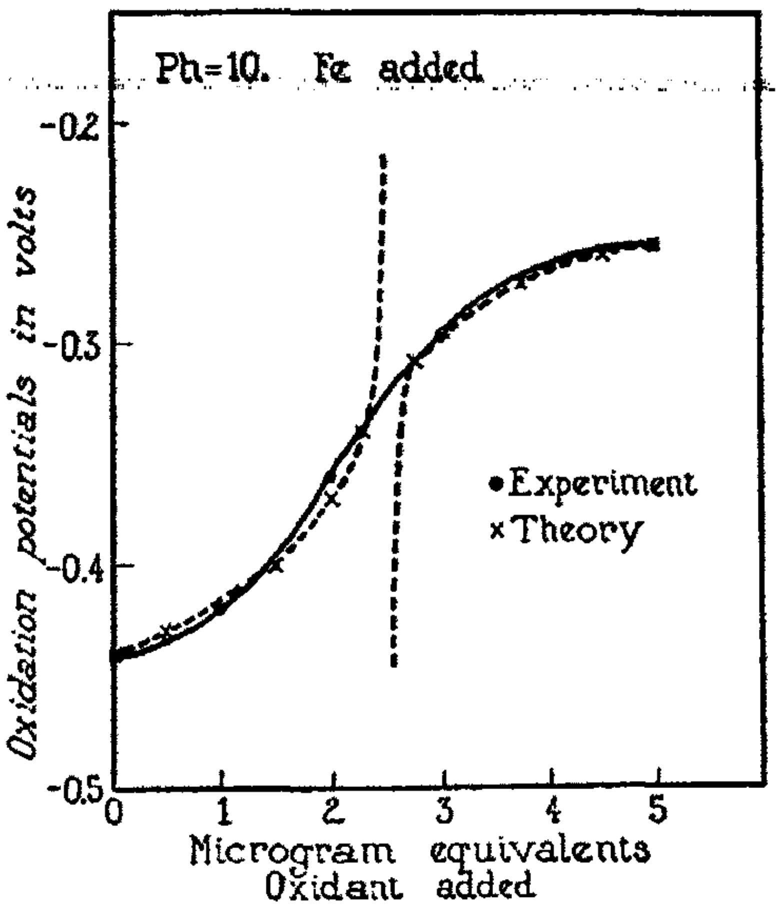

FIG. 2. PEAK POTENTIALS FOLLOWING THE ADDITION OF AERATED DISTILLED WATER

In figures 1 and 2 the solid lines represent actual experimental data, the averages of many single determinations. The dotted lines were plotted from points calculated on the foregoing assumptions. That is, the dotted line curve (figure 1) was constructed according to the equation:

$$P = P_0 - K \log_{10} X \tag{1}$$

where P = peak potential in volts as read after the addition of X units of oxygen, P_0 = potential when X = 1 unit, and K = proportionality constant. In calculating the points for the dotted line curve there are two constants, P_0 and K, to be evaluated, the values of which depend on the arbitrary choice of the value of a unit of added oxidant and for which two simultaneous equations are needed. To supply these the dotted line curve was made to coincide with the solid line curve at the potentials for 0.05 and 10 microequivalents of added oxygen. The broken line curves (figure 2) were also constructed from points calculated from the equation just given, as applied first to an excess of hydrogen and then to an excess of oxygen, X being first the excess of hydrogen, then the excess of oxygen. To construct the dotted line curve for an excess of hydrogen, the dotted line was made to coincide with the solid line curve at the potentials for 0 and 2.25 microgram-equivalents of added oxygen. For the excess of oxygen, the dotted line curve was made to coincide at 3 and 5 microgram-equivalents of added oxygen.

If we admit that in a mildly alkaline solution of glucose, kept out of contact with air, when the concentration of GO^- at the electrode surface is constant and there is no electromotively active oxidant other than GO^-, the potential of a smooth platinum electrode is proportional to the logarithm of the hydrogen concentration, and if we assume that a chemically reversible equilibrium exists between this hydrogen and certain derivatives of glucose, so that the reverse reaction or removal reactions prevent a large accumulation of hydrogen in solution, then it can be shown that the relation between potential and time after the reduction of added oxidants, may be formulated thus:

$$\frac{P^1 - P}{P_0 - P^1} = \frac{\log_{10}\left[e^{\frac{TR}{X_B}} - 1\right] - \log_{10} e^{\left(\frac{TR}{X_B}\right)}}{\log_{10} X_B} \tag{2}$$

and

$$T^1 = \frac{X_B \log_e F}{R} \tag{3}$$

where R = rate of formation of hydrogen, X_B = concentration of hydrogen at equilibrium, P = potential at time T, P_0 = potential for a concentration of hydrogen equal to unity, and P^1 = potential at equilibrium. T^1 =

time necessary for the concentration of hydrogen to be built up to a value so that $1/F$ = fraction of X_E yet to be accumulated.

It is obvious that the above equations will hold only for a period of time during which the electrode potential is proportional to the logarithm of the concentration of hydrogen. There must be no appreciable change in the GO^- concentration at the electrode surface. If an appreciable amount of hydrogen accumulates before the destruction of the last trace of any electromotively active oxidant which may be present other than GO^-, then the equations will hold only after there is no significant amount of such oxidant remaining. Under such conditions the true zero time cannot be directly determined. But by taking several sets of time and potential values, after the oxidant is completely destroyed, enough simultaneous equations can be set up to calculate the equilibrium concentration of hydrogen.

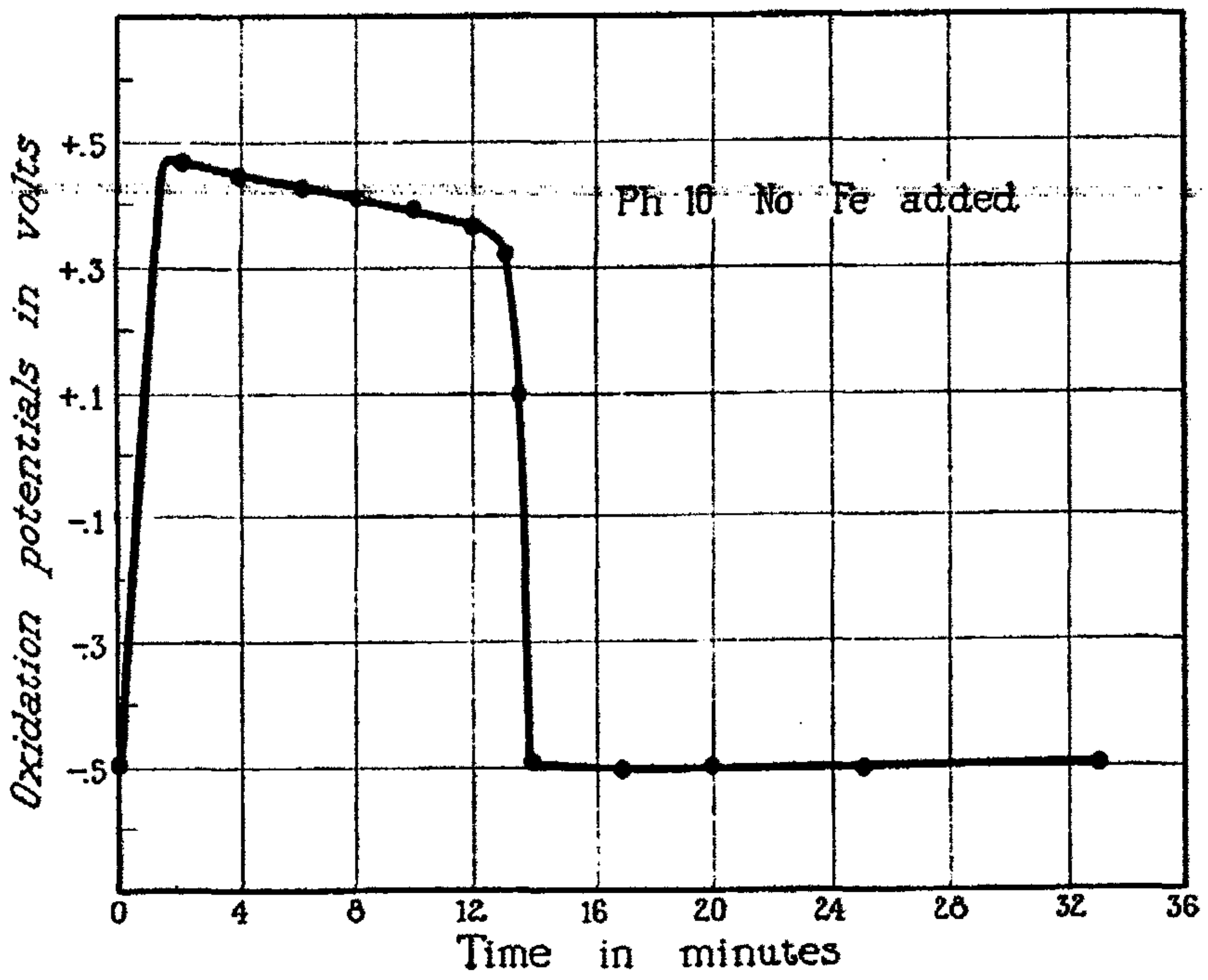

Fig. 3. Drift in Potentials Following the Addition of Potassium Ferricyanide

At pH 10 the reactions are so rapid that the true zero time can be determined directly. Figure 3 shows the drift of potential following the addition of 0.002 gram-equivalent of potassium ferricyanide to a solution of 60

g. glucose + 100 cc. of buffer at pH 10. Thirteen cc. of $N/5$ sodium hydroxide was added with the potassium ferricyanide, which Roepke and Ort found was approximately sufficient to neutralize the acid formed during the reduction of the potassium ferricyanide. Therefore, just at the time the potential was dropping the fastest, the pH was fairly close to 10.

At pH 10, X_E was found by Clifton and Ort to be 2.5×10^{-6}, as indicated also by the point of inflection of the solid line curve of figure 2. R was found by Roepke and Ort to be 9.61×10^{-5} gram-equivalents per minute. Hence T^1 for X to equal $\frac{1}{2}$ X_E is 1.08 seconds. If so, the reaction at this pH should be too fast to permit a detailed checking of the formula by experimentally determined potentials. The curve in figure 3 shows that this is indeed the case, since the drop toward the equilibrium potentials is almost vertical. In taking the readings when the last trace of oxidant had disappeared at about the time represented by 13.5 minutes on this curve, the galvanometer went off scale in a flash, and a few seconds later, if preparations had been previously made, it could again be balanced at a potential around 0.6 volt more negative. Only an approximate titration end point, such as is determined by the technic of Clifton and Ort, is possible under these conditions at pH 10.

According to formula 3, using the values of Clifton and Ort and of Roepke and Ort, the equilibrium concentration for all practical purposes should be built up within ten seconds. It is seen that at this time the potential has indeed reached a value which is about the same as it had before any oxidant was added and near which it remains practically stationary for a number of minutes. This would indicate that the concentration of active reductant had again reached the value it had at the steady state before oxidant was added, and that the potential is indeed proportional to the logarithm of the concentration of hydrogen.

Since the agreement between the experimentally determined rate of potential fall after the reduction of potassium ferricyanide when added to these concentrated glucose solutions at pH 10 and the rate calculated from the above formulas is within the limits of experimental accuracy, the assumptions underlying the development of the formulas seem to be justified under these conditions. At lower values for pH and lower temperatures, where the rates of reaction are so much slower, it should be possible to check theory and experiment in more detail. Since such a check has been found to involve considerable discussion as to the chemical nature of the equilibria involved, this will be left to a subsequent paper. It is obvious of course that the above formulas will apply generally to any electrode potentials which are due to an electromotively active substance which is forming in solution at a steady rate and which in turn is disappearing from the solution at a rate dependent on its own concentration therein, so that ultimately a steady state is reached.

SUMMARY

Evidence has been presented which indicates that an oxygenated derivative of glucose, GO^-, adsorbs to the surface of smooth platinum electrodes and prevents them from acquiring the oxidation-reduction potentials which the concentrations and natures of the oxidants and reductants existing in mildly alkaline glucose solutions would otherwise impart to them. Such adsorption is believed to be the main factor in the recognized variability of the potentials on such electrodes.

Because of the conditions of the former experiments it is pointed out, however, that such adsorption was not an interfering factor in the work of Clifton and Ort in determining the concentration of electromotively active reductant, nor in that of Roepke and Ort in determining the rate of formation of this reductant.

Evidence is also described which indicates that the electromotively active reductant which accumulates to any appreciable extent in such solutions of glucose is molecular hydrogen. On the addition of an excess of oxidants, the hydrogen is oxidized, a glucose oxide, GO^-, is formed, and finally, under the proper conditions, a glucose peroxide, GO_2^-, exists which is electromotively active and gives high oxidation intensities. Finely divided platinum and iron do not affect the rate of formation of the active reductant in these sugar solutions, but do markedly catalyze the reaction between the sugar oxide GO^- and hydrogen and the reaction between these two and certain added oxidants. They activate the oxidants and GO^-, not the hydrogen.

A formula is given which expresses the relation between time and reduction potential following the reduction of added oxidants. It has been checked by experiment at pH 10. By the use of this formula and the rates of formation as determined by Roepke and Ort, the concentration of active reductant at equilibrium can be calculated if the equilibrium potential is known and the reduction potentials are determined at several intervals of time after the reduction of added oxidant is complete.

Although data are given in this paper only for glucose, these conclusions apply generally to many of the common sugars.

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THE HYDRATION OF THE CRYSTALLINE FIBERS OF SOAP CURD

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Received February 23, 1934

The commonest occurrence of soap is in the form of curd fibers embedded in a liquid crystalline solution, as in many household soaps. Some toilet soaps consist almost exclusively of curd fibers. These solid and concentrated forms of soap are the most difficult to characterize scientifically, and their nature is most open to dispute (5).

Curd fibers, by x-ray evidence (12, 13, 14, 15), are crystalline, exhibiting three spacings as distinguished from the one of liquid crystals. They have been shown to consist of hydrated neutral soap (4). They exhibit a definite solubility which is, however, very greatly dependent upon temperature and to a certain extent upon previous history. In our phase rule studies (6) we have found it possible to treat them as a phase or, rather, as a series of phases, although this is considered erroneous or incomprehensible by others.[2] This is partly due to the fibers not being massive; for although they may be centimeters long, they are finely microscopic or, more usually, ultramicroscopic in breadth and thickness. They thus present a large surface available for sorption, and all electrolytes are noticeably sorbed by them. Even saturated sodium chloride solution, which completely displaces other more dilute electrolytes from the curd fibers, does not prevent all non-electrolytes so far studied from being appreciably sorbed, glycerol being the sole exception.

One highly reproducible measurement has been made by four previous independent methods (3, 7, 9, 11). Sodium palmitate fibers at 90°C. in the presence of a saturated solution of sodium chloride are found to contain 2.1 mols of water to 1 mol of sodium palmitate. They also contain between 1 and 3 per cent of sodium chloride. Thus the strong negative sorption of sodium chloride by sodium palmitate is in reality a slight positive sorption by the hydrated fibers.

Using glycerol, Bennett (1) found that at room temperature the hydrated

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[1] Experimental work carried out at Bristol University, England, in 1923–1927.

[2] For example, Ostwald and Erbring: Kolloidchem. Beihefte 31, 345–46 (1930); however, they are doubtless depending upon their own assumption, "Da der Wassergehalt dieser Kernfasern zweifellos kontinuierlich variiert."

sodium palmitate fibers separating from ordinary isotropic (0.25 N_w) solution have the composition $NaP \cdot 10H_2O$, whereas those separating from more concentrated (1.0 N_w) anisotropic liquid solutions (liquide à conique) exhibit an empirical formula $NaP \cdot 4.3H_2O$.

The present communication employs the dew point method of measuring vapor pressure in studying the hydration of curd fibers of sodium palmitate and sodium laurate with and without the presence of a saturated solution of sodium oxalate. The results are unexpected in that they appear to indicate definite hydrates or amounts of water of crystallization.

EXPERIMENTAL METHOD

The dew point apparatus is that first designed by Cumming (2) with the essential modifications by McBain and Salmon (8) which convert it into a differential method. It is shown in diagram in figure 1.

A highly polished silver test tube is fitted with a rubber stopper in which is inserted a thermometer, reading to 0.01°C., and two glass tubes through which a rapid current of water is circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube is held in a large rubber stopper fitted into an outer glass vessel which contains the close-fitting, thin-walled shell holding the solution or curd to be studied. The top of the outer vessel rises about one inch above the stopper, so that the closed space is completely immersed in distilled water in the transparent thermostat. A glass capillary tube, sealed to a stopcock, passes through the stopper holding the silver tube and may be connected with a water pump and the outer vessel thus evacuated if required. The glass outer vessel should be as small as possible so that equilibrium can be quickly attained.

The silver tube should be kept highly polished by a silversmith. Hand polishing requires practice. The motion should be along the length of the tube so as to avoid any disturbing transverse scratches. For cleaning, the tube was immersed overnight in freshly distilled thiophene-free benzene and lightly polished with silk which had been extracted with benzene. The effects of traces of hydrogen sulfide have to be removed by polishing with jeweler's rouge. The device of preventing formation of dew on a diagonal portion of the lower part of the silver test tube by coating it with an invisible film from boiling conductivity water was used in the manner originated by McBain. Illumination has to be carefully adjusted for optimum visibility of the boundary between the bright surface and that dimmed by incipient formation of dew. Too much dew may necessitate recleaning.

The silver tube was adjusted to 1.0°C. above the temperature of the thermostat before assembling as in figure 1. To hasten attainment of equilibrium the outer tube was evacuated. Under good conditions the difference between appearance and disappearance of dew was only 0.03°C., the mean being taken as the dew point. The zero correction, for differences between thermometers, and personal error, was found by one of us (H. I. B.), but not by previous workers, to depend slightly upon the condition of the silver tube, which was therefore subjected to an exact routine of cleaning and treatment. It is determined by measuring the dew point lowering of conductivity water itself; these measurements were repeated at frequent intervals as a check.

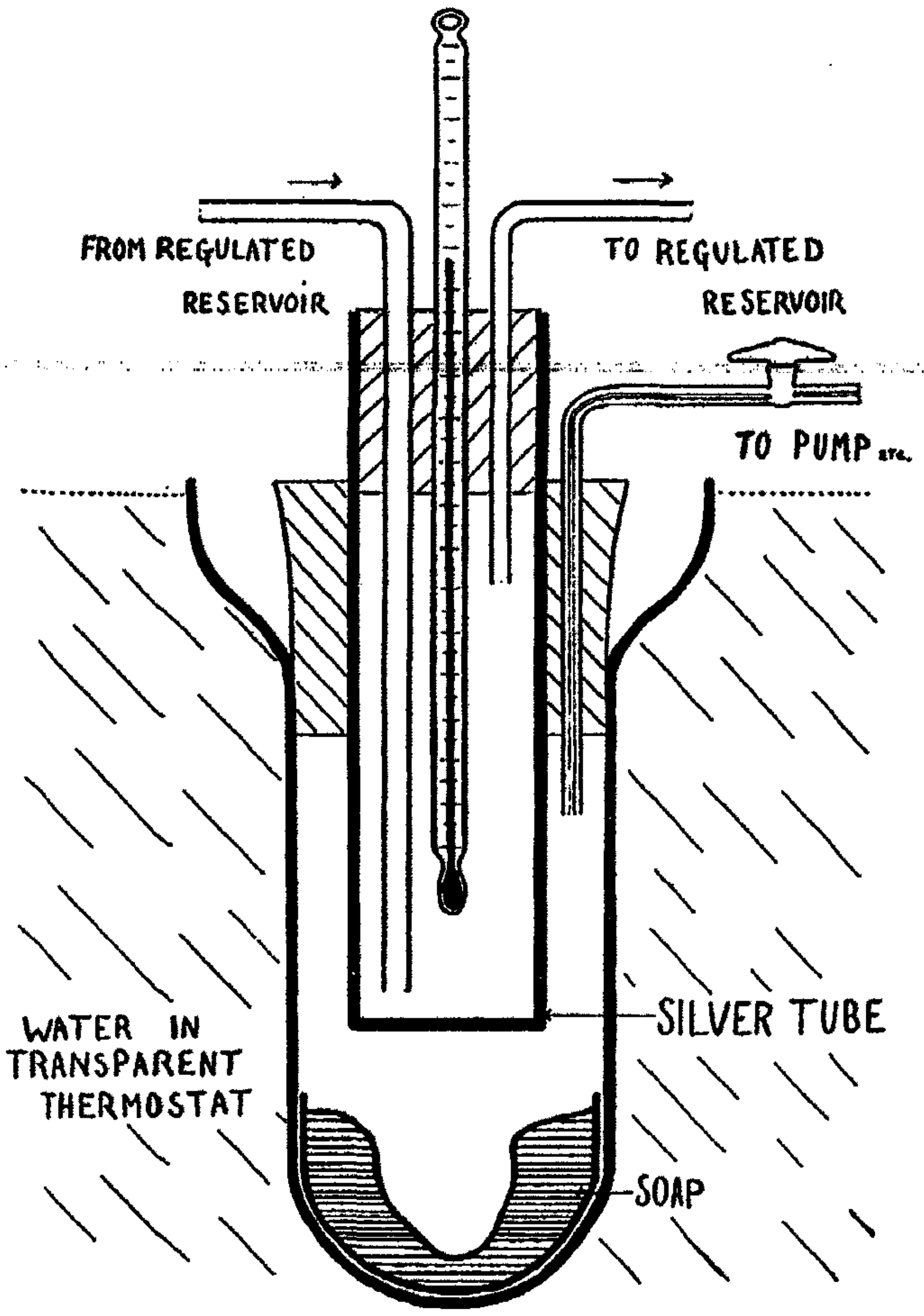

FIG. 1. DEW POINT APPARATUS FOR STUDYING VAPOR PRESSURE OF SOLUTIONS OR SOLIDS CONTAINING WATER

To insure avoidance of false equilibria with viscous solutions it is necessary to shake or stir the specimen being measured. With curds the most satisfactory device is to allow the curd to form in the vessel where practicable and then to cut away the upper surface and the middle portion of the curd itself as shown in figure 1. Water diffuses better in this way than when the curd is a heap of separate lumps. The curd is allowed to remain in contact with the closed (evacuated) vapor space for several hours before taking a measurement. In the later experiments not more than 30 mg. of water was removed from a curd at a time; or, if large amounts were removed, the curd was left for a week in a closed vessel to recover internal equilibrium.

Dehydration of the curd within the dew point apparatus was found inadvisable and was rejected in favor of dehydrating the curd by placing its container in a vacuum desiccator and weighing from time to time. The chief disadvantage is that the exact composition at which a break occurs in the vapor pressure is missed and has to be surmised from inspection of the graphs of dew point lowering against gross composition of the curd.

The curds were subsequently analyzed by the methods and using the precautions described in previous communications. They were first dissolved in boiled-out neutral water, decomposed with excess of acid, the fatty acid titrated in 80 per cent alcohol, and the aqueous filtrate with standard alkali. Then if sodium oxalate was present, it was determined with permanganate.

A quicker method used in the later experiments on curds containing no oxalate was complete dehydration to constant weight. Thus with curd 25A (H. I. B.) complete analysis of 0.4232 g. of such completely dehydrated curd yielded 0.4230 g. of sodium palmitate. Thus from the weight at any time, the amount of water present was known by difference.

Each dew point lowering recorded is the mean of from six to twenty individual readings of which many thousand were required for the present work.

Results in presence of saturated sodium oxalate[3]

Sodium oxalate crystals were present in excess for the purpose of serving as an indicator to show when the last amount of free solution just evaporated. Up to this point the dew point has to remain constant, but thereafter any water withdrawn comes from the dry fibers of the hydrated soap curd and the vapor pressure falls suddenly.

The sodium palmitate and sodium laurate were special preparations made for us by Kahlbaum. They were dissolved by heating in a Jena glass-stoppered bottle at 90°C. until the solution was homogeneous. On cooling, a viscous pale yellow gel formed and became a solid white curd. After adding excess of Kahlbaum sodium oxalate, the solution was heated for twelve hours at 90°C., well shaken, and cooled to a solid white curd at 24°C. In some of these experiments the stirring or time allowed for equi-

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[3] Experiments by L. S. S.

librium was insufficient, but the position of the break in the vapor pressure curve should be significant.

Dew point lowerings observed with saturated solutions of sodium chloride were 4.83, 4.84, 4.83, and 4.83°C. as compared with 4.82°C. in a mixture of solid salt and saturated solution. A similar mixture of sodium oxalate and saturated solution gave 1.46 and 1.45°C., which is therefore the constant reading to be expected until all water other than that actually held by the fibers is gone. The following results were obtained with the second specimen of soap curd, prepared from 0.5 N_w sodium palmitate containing excess of sodium oxalate:

Mols H_2O to 1NaP..	107	67	57	40	6	2.9	1.42	0.77	0.22
Dew point lowering, °C.	1.44	1.45	1.44	1.44	1.45	1.46	3.62	4.57	5.17

Other data from results with three other similar curds were:

Mols H_2O to 1 NaP	2.58	2.23	1.24	1.28
Dew point lowering, °C.	1.68	3.57	4.54	4.07

From the complete graphs for three curds the hydration of sodium palmitate fibers formed from 0.5 N_w solution containing excess of solid sodium oxalate was estimated as 2.52, 2.70, 2.58; mean, 2.6 mols H_2O to 1 mol sodium palmitate.

McBain and Salmon (9) obtained for the hydration of sodium palmitate prepared from 1.0 N_w solution in the presence of excess of sodium chloride the same result as that found here, namely, $NaP \cdot 2.60H_2O$, as compared with the value $NaP \cdot 2.16H_2O$ at 90°C. and $NaP \cdot 2.36H_2O$ at 50°C. Inspection of their table 1 for highly dehydrated curds shows that beyond the region of this break they too failed to obtain reproducible results; and all existing data for further dehydration are too uncertain to distinguish definitely between sorption, or a further definite hydrate, or both. We found by trial that a saturated solution of sodium oxalate may be made to yield only a fraction of its true dew point lowering by carefully avoiding any stirring. Water is forcibly abstracted to form the dew upon the silver; this is then returned to the surface of the solution, rendering it dilute. Similarly, with dried curd the dew point lowering may not be nearly great enough or may be too great, depending upon which factor preponderates, this, or as in these experiments, insufficient time for internal equilibrium.

It seems possible that the real composition of these curds formed in the presence of the two saturated salts, whose dew point lowerings are 1.45 and 4.83°C. at 20°C. (and 6.49°C. at 90°C.), is really the definite hydrate $NaP \cdot 2H_2O$; and that the actual composition so often confirmed at 90°C., $NaP \cdot 2.1H_2O$, as well as that at 20°C., $2NaP \cdot 2.6H_2O$, is due to superimposed sorption. It will be noted in the sequel that the gross composition, $NaP \cdot 2.6H_2O$ at 20°C. has been observed again even in the absence of salt.

Sodium laurate proves, as expected, to be much less hydrated than sodium palmitate. The break in the horizontal vapor pressure curve, which is followed by a great lowering, leaves as a result of two imperfect series the composition of the curd as $NaL \cdot 1.2H_2O$. This is less than that found by McBain and Salmon at 90°C. in the presence of saturated sodium chloride, namely, $NaL \cdot 1.80H_2O$.

Results with sodium palmitate curds in the absence of salt[4]

In two preliminary experiments (by L. S. S.) on the dehydration of 0.5 N_w sodium palmitate curd at 23°C. it was found that the dew point observed was steadily lowered until at the composition just above $NaP \cdot 9H_2O$ there was a sudden break, followed by a much more rapid lowering of the dew point. This compares with the value $NaP \cdot 10H_2O$ found by Bennett at 20°C. from the negative sorption of glycerol in 0.25 N_w curd.

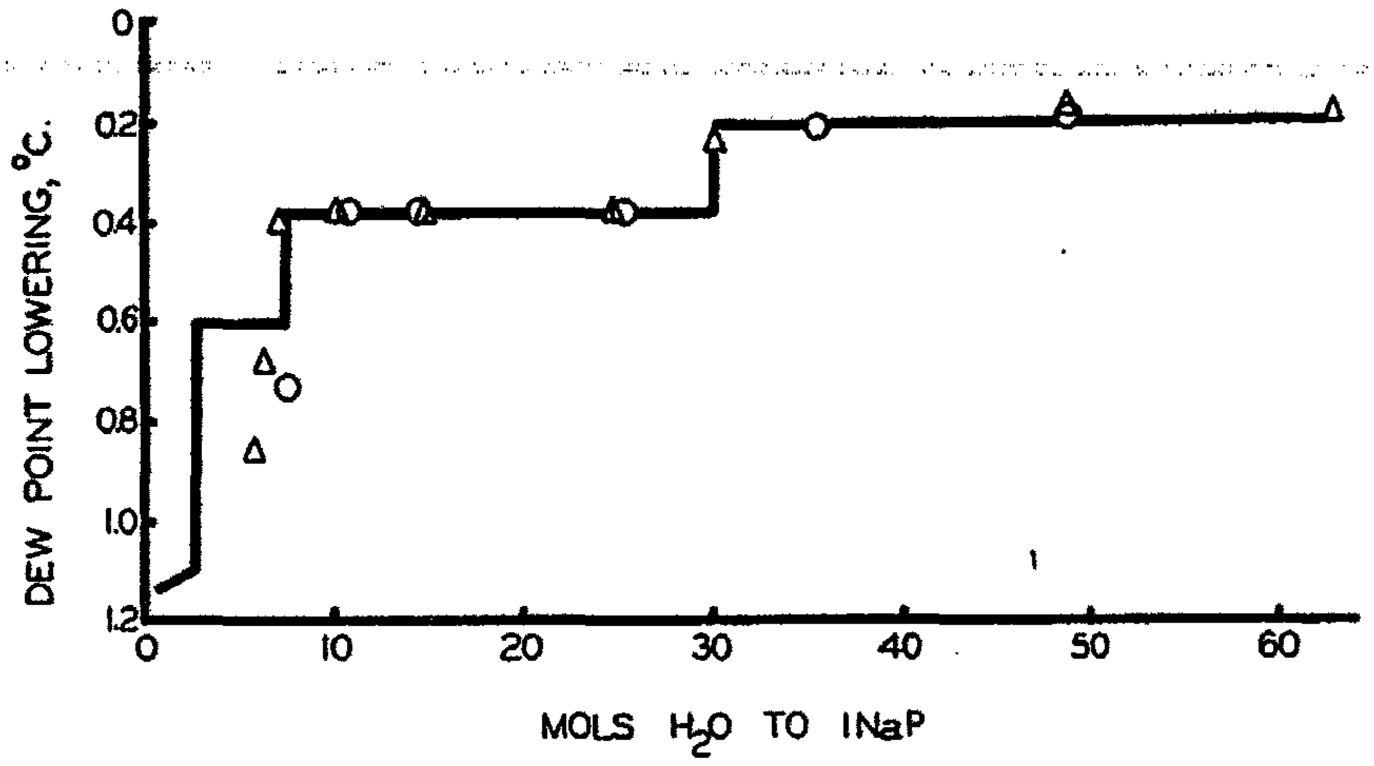

FIG. 2. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 0.5 N_w SODIUM PALMITATE

In developing the more careful technique required to follow up this result, one of us (H. I. B.) became convinced that the curves of vapor pressure against composition were essentially phase rule diagrams which consist of horizontal and vertical portions. As soon as exceptional care was taken in studying the vapor pressure of a particular curd, and much more opportunity was afforded for the attainment of equilibrium, the sloping curves of previous work were replaced by others such as are shown in figures 2, 3, and 4. In other words, soap curds appeared as definite hydrates of

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[4] Experiments by H. I. B. except where otherwise noted.

definite composition and reproducible properties. The data seem fairly convincing, although this result was unexpected. It goes far beyond a mere demonstration that curd fibers contain bound water, a fact which was already established beyond peradventure even without the additional evidence given in both parts of this paper. Some way must be found for accounting, in the interpretation of x-ray data, for the water which is certainly present, perhaps through an arrangement of the water molecules on exposed surfaces.

The chief point at issue, after noting the fact of the presence of water in the dried fibers,[5] is as to whether the vapor pressure or dew point lowering curves are continuous, as in sorption, or discontinuous as in phase rule studies of definite hydrates, as drawn in figures 2 to 4. In the latter case the vapor pressure must remain constant until a hydrate has just been removed by dehydration, whereupon the horizontal line must drop to a new value as soon as again there are two solid phases in equilibrium with the vapor. The position of the break then gives the composition of the hydrate.

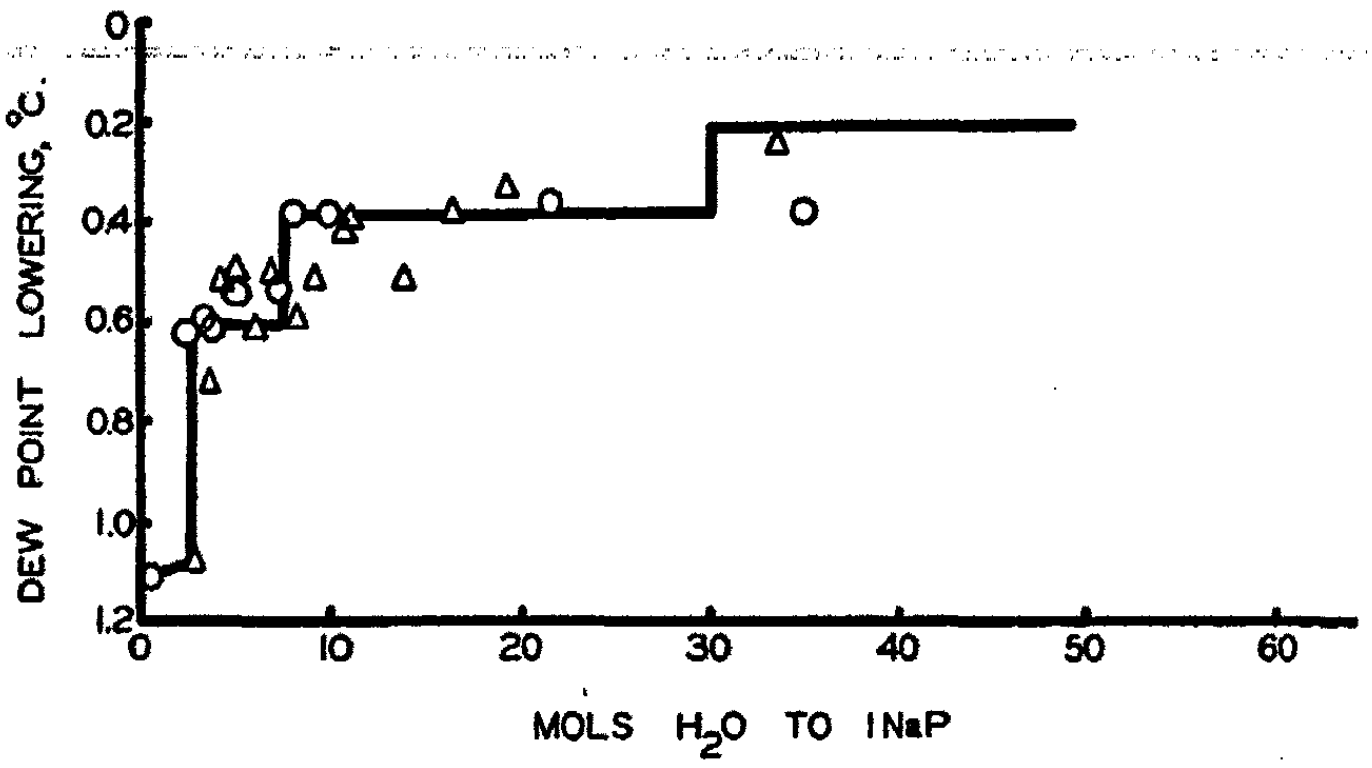

FIG. 3. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 0.5 N_w SODIUM PALMITATE

The first experiment was with 0.25 N_w curd of sodium palmitate at 20°C., showing a break at least at about NaP·$8H_2O$, although the curves are

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[5] It will of course be noted that the dew point lowering corresponds to that of a highly concentrated solution, no such solution being present; the expressed mother liquor from the original wet curd being less than $N/50$, it was removed by the previous evaporation.

otherwise not definitive. The readings of gross composition and dew point were:

Mols H_2O to 1 NaP......	102.3	77.5	43.3	19.3	13.7	8.6	7.3	6.6
Dew point lowering, °C...	0.19	0.18	0.25	0.30	0.31	0.31	0.47	0.60

The data for 0.5 N_w curds of sodium palmitate are given in figures 2 and 3, each of which records two independent series. The lines for all four are necessarily drawn in identical position in order to be consistent. They show a possible unproven break at $NaP \cdot 30H_2O$ and another undoubted one at $NaP \cdot 8H_2O$, or perhaps in one case nearer $NaP \cdot 10H_2O$. Only in the fourth experiment in figure 3, indicated by triangles, less reproducible results were obtained because the curd was employed, not in coherent form, but broken into pieces which did not come so readily into equilibrium. It is remarkable that in all cases the vapor pressure lowering of the dried curd between the compositions $NaP \cdot 30H_2O$ and $NaP \cdot 9H_2O$ is 0.38°C.

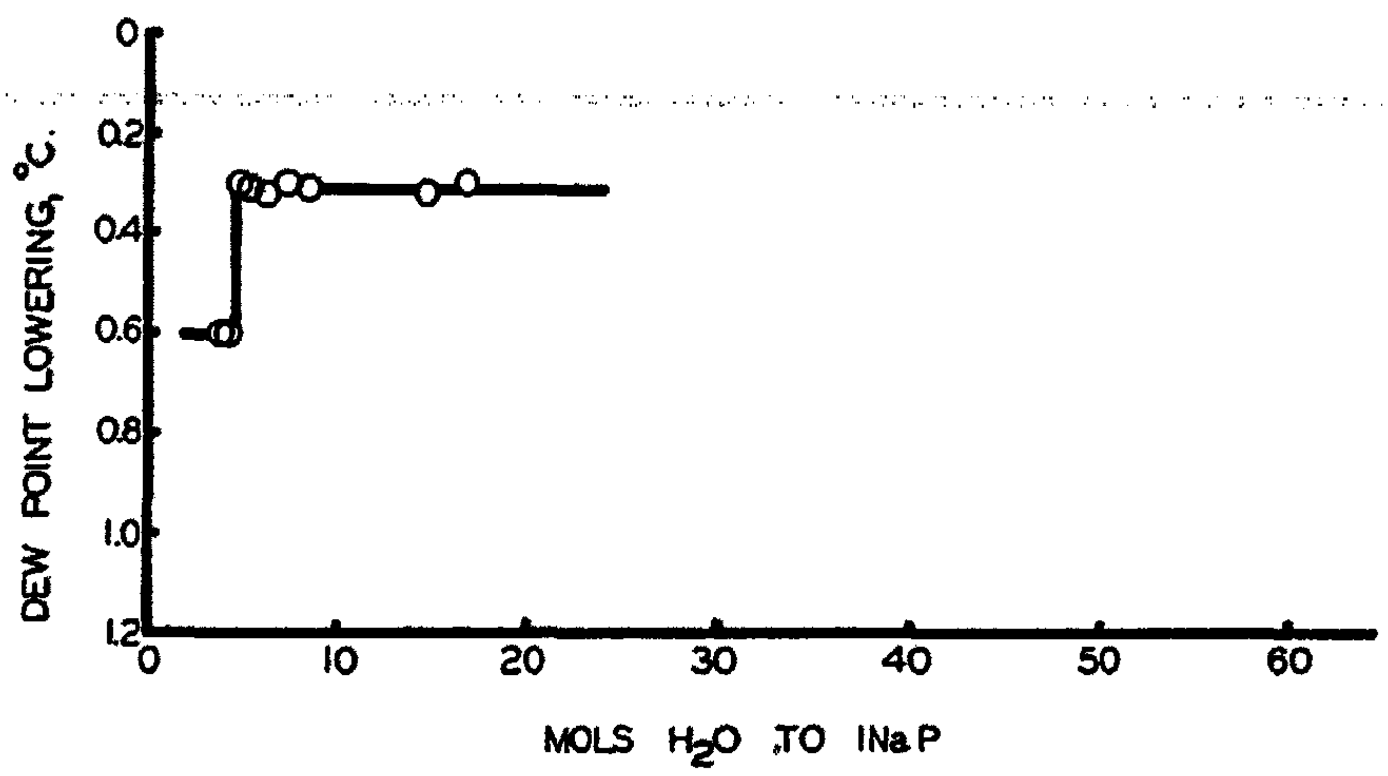

FIG. 4. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 1.0 N_w SODIUM PALMITATE

It seems also possible for one curve, studied sufficiently far, that the composition $NaP \cdot 2.6H_2O$ found in the earlier part of the paper corresponds to a break.

The whole point of figures 2, 3, and 4 is that, unexpectedly, they show breaks and that, furthermore, the position of the break for figures 2 and 3 at $NaP \cdot 8\text{–}10H_2O$ and the different one upon figure 4 agree with the hydrations previously published for these two different kinds of curd upon the basis of the method of indirect analysis. We can only repeat that these breaks, which we did not expect, have appeared only in those experiments in which the greatest care was taken to minimize false equilibrium.

Figures 2 and 3 for 0.5 N_w curds are in striking contrast to figure 4 for 1.0 N_w curd. Bennett had already proven by the glycerol method that for the former the curd had the composition $NaP \cdot 10H_2O$ and for the latter $NaP \cdot 4.3H_2O$, one having separated from isotropic soap solution and the other from liquid crystalline anisotropic smectic soap solution (liquide à conique).

The first experiment with 1.0 N_w sodium palmitate curd showed these to be still more difficult to study, but there was a break at $NaP \cdot 4.6H_2O$. The next and final experiment is that given in figure 4. The curd was allowed to dehydrate itself by being kept for some time in a fairly large closed vessel until it had lost not more than 0.02 g. between successive measurements. The dew point lowering is constant at 0.31°C. over a wide range of composition with a very definite break between $NaP \cdot 4.4H_2O$ and $NaP \cdot 4.9H_2O$. This is in excellent agreement with Bennett's wholly independent finding by the use of glycerol as a reference substance with analysis of exuded mother liquor.

We refrain in this place from discussion of the results obtained under the very different conditions at 90°C. on solutions of very different antecedents and properties. At 20°C. Bennett's results were based upon the assumption that no sorption occurred and that the concentration of glycerol in the expressed mother liquor was due solely to combined water within the curd fibers. However, if there is negative sorption of glycerol in the glycerol-curd fiber interface as there is in the glycerol-air interface, this could make Bennett's results slightly higher than the true hydration. The unique property of glycerol of not being sorbed by soap curd is not paralleled by its solubility in soap solution, for in unpublished experiments on partition between neat soap and lye it is found that the proportion of glycerol in the neat soap is several times that of any electrolytes present.

SUMMARY

The dew point method has been used at room temperature to demonstrate the presence of bound water in dried fibers of soap curd. When formed in the presence of a saturated solution of sodium oxalate, sodium palmitate fibers have the composition $NaP \cdot 2.6H_2O$. It would even appear possible that there are definite hydrates of sodium palmitate, including $NaP \cdot 8H_2O$ and, possibly, $NaP \cdot 2.6H_2O$ and $NaP \cdot 30H_2O$, although these results may be partially overlaid by sorbed water. Curd fibers obtained from liquid crystal anisotropic solutions contain half as much water as those from ordinary isotropic solutions. The behavior of soap curd, which is due to crystalline, although often ultramicroscopic, fibers, is wholly different from that of any gels or jellies.

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THE SYSTEM PYRIDINE-ACETIC ACID. II

FUSION POINTS

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Received April 19, 1934

INTRODUCTION

In a previous paper by one of the authors (10) the viscosities of pyridine–acetic acid mixtures were reported with a maximum viscosity for mixtures in the neighborhood of 80 mole per cent acetic acid. A similar behavior for this same system has been reported by Tsakalotos (11), Faust (5), and Dunstan (3).

While it is generally conceded that the existence of a maximum viscosity in mixtures indicates the formation of some type of compound or complex, it has been found that certain systems may show a maximum viscosity without compound formation between the components of the system. Further, it has been observed that the absence of a maximum viscosity does not necessarily indicate the absence of compounds (4).

In the viscosity data for the system pyridine–acetic acid, reported by Swearingen and Heck (10), it was shown that the maximum viscosity for the mixture in the neighborhood of 80 mole per cent acetic acid was quite pronounced at ordinary temperatures and was still very much in evidence at temperatures as high as 80°C. It was also shown that the composition at which this maximum viscosity appeared was practically independent of the temperature, remaining constant at about 80 mole per cent acid over the range of temperatures studied. In view of this rather peculiar behavior, the present authors have attempted to secure additional experimental data on this system, so that the nature of these mixtures having large viscosities may be more definitely characterized.

EXPERIMENTAL PROCEDURE AND DATA

The procedure adopted as most likely to give the desired information was to determine the melting point–composition relations for this system. The presence or absence of compounds in this system should be readily revealed by the melting point-composition diagram.

The theoretical basis and experimental technique of this procedure have been adequately discussed by Kendall (6). The melting point-composition relations do not always give a positive means of correlating compound formation with abnormally great viscosities. Kurnakov, Krotkov, and Oksmann (7) find that some compounds are revealed on the melting point–composition diagram and not on the viscosity–composition diagram. The reverse of this case has also been found to be true. O'Conner (8) states that the fusion diagram fails to indicate compound formation in the system methylaniline–acetic acid, but that the considerable heat evolved on mixing these components indicates chemical combination. Further, Bramley (1) finds that the freezing point–composition diagrams for several phenols with certain organic acids do not indicate any equimolecular compounds, but he argues that they must exist.

A standard grade of glacial acetic acid was first repeatedly recrystallized and finally treated with phosphorus pentoxide and distilled under reduced pressure. A second quantity of the acid was purified by the method of Rüdorff (9). Both products showed a freezing point of 16.3°C.

A standard grade of pyridine was subjected to repeated fractional distillation, using a long Hempel fractionating column. The fraction finally collected for use boiled within a range of 0.5°C. This product was then allowed to stand over solid sodium hydroxide and then refractionated. The final product showed a melting point of −43.5°C.

From these purified materials, mixtures were made covering the entire range of composition. The compositions were expressed in mole per cent.

The freezing or melting temperatures were determined with either mercury or toluene thermometers, depending on the freezing points of the material under investigation. These thermometers were calibrated by means of a standard thermometer calibrated by the Bureau of Standards and by fixed points.

A small quantity of the mixture to be investigated was placed in a small closed glass tube along with the thermometer and stirring device. The tube was then placed in a freezing bath of solid carbon dioxide and ether, contained in a Dewar vessel. The mixture was frozen and the sample tube then removed from the freezing bath. The temperature of the sample was permitted to rise slowly, and the mixture was stirred uniformly after the first appearance of the liquid phase. The temperature at which the last small crystals disappeared was taken as the melting point of the sample. This procedure was repeated several times on each sample, the final melting points being quite reproducible.

The procedure, as outlined, was adopted after it was found that many of the mixtures exhibited a large degree of supercooling before crystallization could be induced. This condition was most marked in the region of high viscosity. In the case of samples of composition falling in the high viscosity range, in order to prevent the supercooled liquid from taking a glass-like "set," it was necessary to seed to induce crystallization. Similar conditions have been observed in other systems (2).

DISCUSSION OF EXPERIMENTAL RESULTS

The fusion diagram, figure 1, shows definitely the existence of two compounds and two eutectic mixtures. One eutectic mixture occurs at 30 mole per cent acetic acid with a melting point of −67.5°C.; the other at 66 mole per cent acid with a melting point of −59°C. One compound occurs at 50 mole per cent acid with a melting point of −48°C., corresponding to the simple salt, pyridonium acetate. The other compound has an incongruent melting point, above −42°C., as indicated by the extrapolated (broken) line. The composition of this latter compound is probably either 80 or 83.3 mole per cent acid, since these compositions correspond to the compounds $C_6H_5N \cdot 4CH_3COOH$ and $C_6H_5N \cdot 5CH_3COOH$, respectively.

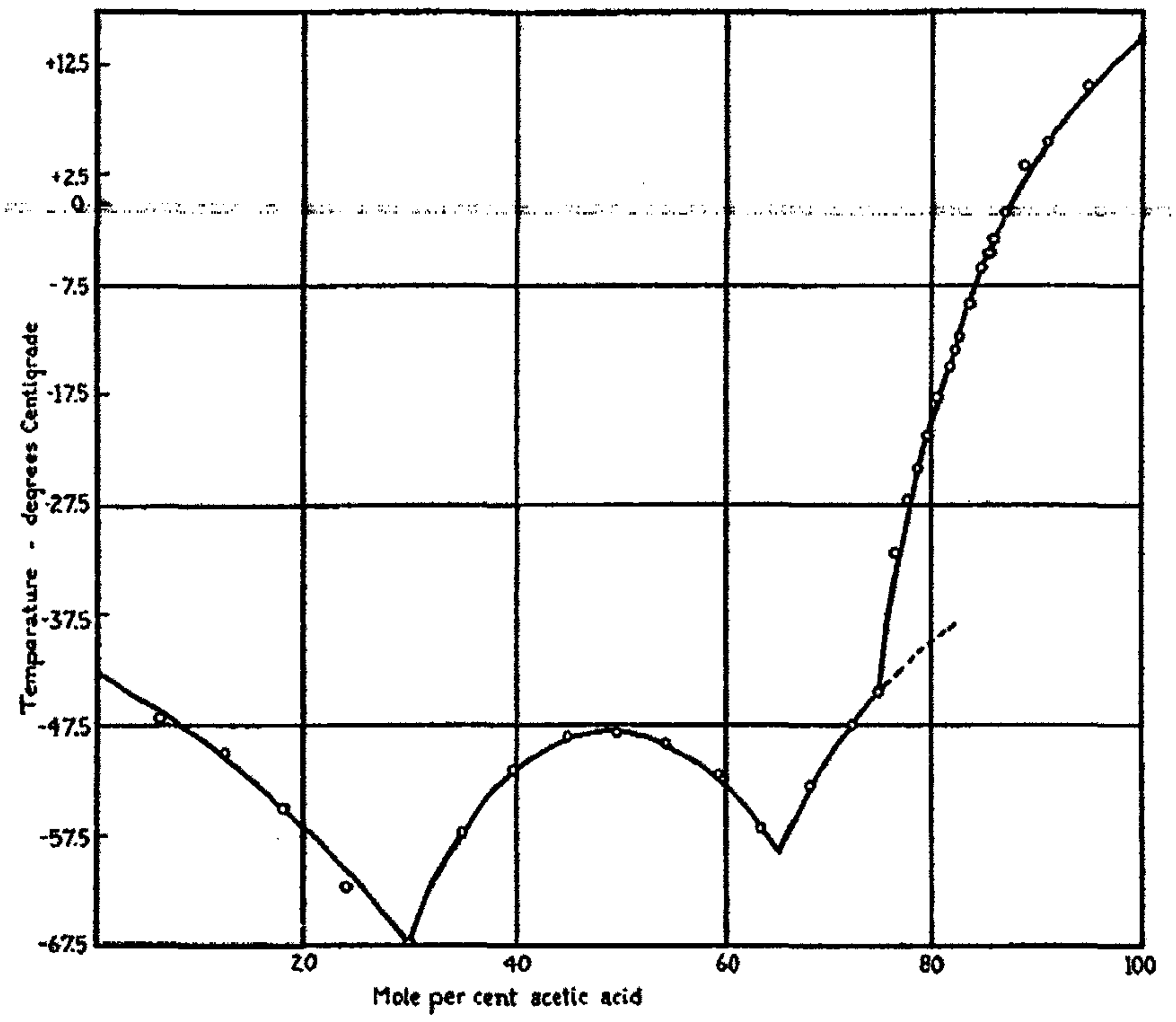

FIG. 1. MELTING POINT–COMPOSITION DIAGRAM FOR THE SYSTEM PYRIDINE–ACETIC ACID

The compound melting in the neighborhood of −42°C. crystallizes from mixtures which fall in a very limited concentration range,—66 to 75 mole per cent acid. The fact that this compound is completely dissociated at temperatures above its melting point makes it seem highly improbable that this compound, as such, is responsible for the maximum viscosity shown in this region. The abnormally high viscosity is still very much in evidence at temperatures considerably more than 100°C. above the melting point of this compound. No irregularity occurs in the viscosity–composition relation at the composition corresponding to the simple pyridonium acetate.

Thus, the melting point–composition diagram for this system indicates the existence of two compounds, one of which is indicated by the viscosity–composition relationship. While there is a certain degree of coincidence in the probable composition of this compound and the composition of the mixture having maximum viscosity, this cannot be due to the compound itself. The agreement may be accidental or may be due to some peculiarity of this dissociated compound. The fact that the simple stable compound formed has no noticeable effect on the viscosity of the system, indicates that compound formation is neither the necessary nor the sufficient condition for a maximum viscosity to occur.

TABLE 1

Melting points of pyridine–acetic acid mixtures

MOLE PERCENT ACETIC ACID	MELTING POINT	MOLE PERCENT ACETIC ACID	MELTING POINT
	degrees C.		*degrees C.*
0.000	−43.5	77.722	−26.9
6.345	−47.1	78.698	−23.8
12.566	−50.6	79.734	−20.9
18.529	−55.3	80.771	−17.7
24.359	−62.3	81.543	−14.7
29.943	−67.5	82.221	−13.3
35.225	−57.4	82.669	−11.9
40.268	−51.6	83.720	−9.2
45.440	−48.6	84.773	−5.8
50.004	−48.2	85.234	−4.5
54.890	−49.1	85.894	−3.0
59.594	−52.3	86.470	−0.6
63.927	−56.7	86.790	0.0
68.202	−52.9	88.568	3.7
72.438	−47.5	90.710	6.6
74.790	−44.5	94.834	10.95
76.256	−31.8	100.000	16.3

SUMMARY

1. The melting points of various mixtures of pyridine and acetic acid have been determined and the melting point–composition diagram constructed.

2. The melting point–composition diagram for this system indicates the presence of two compounds, $C_6H_5N \cdot CH_3COOH$ and $C_6H_5N \cdot 4CH_3COOH$ (or $C_6H_5N \cdot 5CH_3COOH$), melting at −59°C. and about −42°C., respectively.

3. The simplest of these compounds revealed on the melting point diagram is not revealed on the viscosity–composition diagram. While the more complex compound is revealed on the viscosity–composition diagram, its responsibility for the maximum viscosity occurring here, is, to say the least, questionable.

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INTERPRETATION OF THE PRESSURE-VOLUME-TEMPERATURE RELATIONS OF SINGLE AND COMPOSITE GASES

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Received March 27, 1934

In a recent article (3) is given an equation which adequately describes the *P–V–T* relations of several important gases over a pressure range from 1 to 3000 atmospheres, and over a temperature range from 0°C. to 200°C. The purpose of the present article is to show that the equation is equally applicable to the *P–V–T* behavior of mixtures of those gases, and over a much greater temperature range. The results are presented in two condensed tables.

The data for hydrogen, the mixture of hydrogen and nitrogen, nitrogen, and carbon monoxide are taken from recent articles by Bartlett (2); those for carbon dioxide from Amagat (1). In order to economize on space all the original data are omitted, since they are easily accessible. The value of V_∞ for the 3 to 1 mixture of hydrogen and nitrogen gases was obtained from the additive relation,

$$1/V_\infty = 4/(3V_\infty \text{ of } H_2 + V_\infty \text{ of } N_2)$$

The value of V_∞ for carbon monoxide was read off on the curve $1/V$ vs. $\log P$ as described in the previous paper. In the case of carbon dioxide, however, the data do not extend sufficiently far to determine the point of inflection, as a glance at figure 2 will show. It was therefore found necessary to resort here to the less reliable method already mentioned (3), namely, the calculation of V_∞ from the density of the substance in its solid state. In the literature it is stated that the density of carbon dioxide "glass" is 1.56 at about 194° Absolute. From this value $1/V_\infty$ was found to be approximately 800.

DISCUSSION OF THE CONSTANCY OF K

In discussing the constancy of K in the given equation,

$$(V_1 - V_\infty)/(V - V_\infty) = P^K$$

it may be pointed out that a change in K of 0.1 per cent produces a deviation of about 0.4 per cent in the calculated volumes or densities of a given gas. Hence, a 2 per cent or 3 per cent change in K would render the equation useless for interpolation or extrapolation purposes, provided there were a definite trend in the K values. If, however, the values of K varied more or less alternately to the extent of 2 per cent or 3 per cent, it would merely indicate large experimental errors, which might be inherent in the method of measurement. Thus the K values for hydrogen gas at 0°C. calculated from Amagat's data vary among themselves to the extent of 1 per cent, corresponding to a 4 per cent error in the original measurements; while in the K values from Bartlett's data, obtained presumably under like conditions, the largest deviation is only 0.1 per cent, corresponding to a maximum experimental deviation of only 0.4 per cent. In other words, Bartlett's results, *in this case*, appear to be ten times as accurate as the results of Amagat, yet each investigator claims the same degree of average accuracy, about 0.2 per cent; this is true for Bartlett's results, but not for those of Amagat. In this connection it may be mentioned that the ultimate molal volume for hydrogen gas calculated from Amagat's data is about 15 cc., while if calculated from Bartlett's data the ultimate molal volume is about 16 cc.; this value is used in the present calculation. Furthermore, the K values of hydrogen calculated from Bartlett's data indicate that

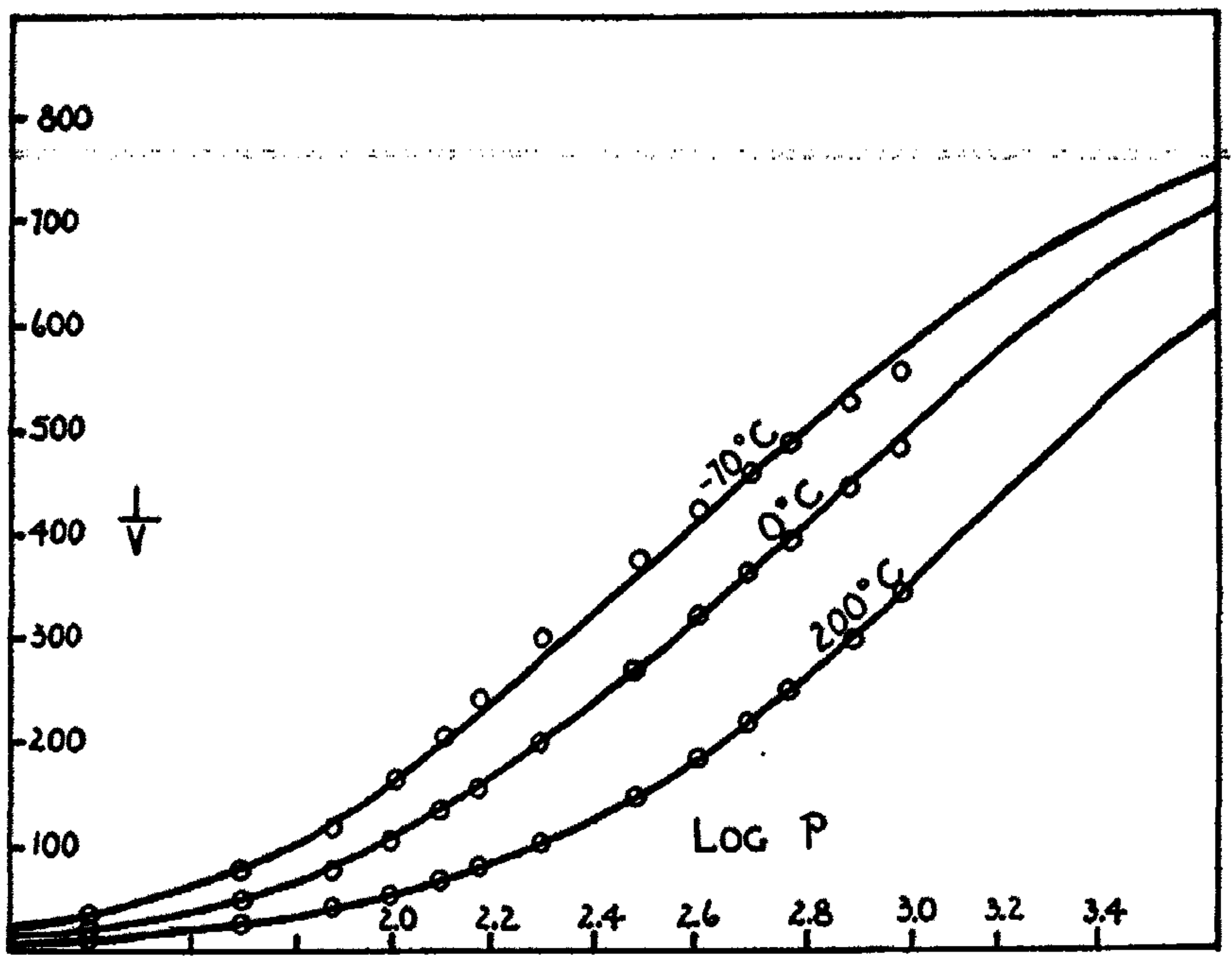

Fig. 1. *P-V-T* Relations of Carbon Monoxide Gas

hydrogen, instead of being an exception as noted in the paper cited (3), behaves like all other gases; that is, the average K values for the different temperatures are never less than unity. It is also interesting to note that the K values increase with the molecular weight of the gas (see figure 3), approaching unity at high temperature for the several gases studied. This being the case, it follows that K cannot be less than unity, since hydrogen is, at present, the lightest of all gases.

In the case of nitrogen gas the experimental results from both sources seem to be of about the same degree of accuracy, namely, 2 per cent to 3 per cent. The largest experimental deviations appear in Amagat's data for carbon dioxide gas; but the K values for this gas at 0°C. remain fairly constant up to the point of liquefaction of the gas, where the curve becomes discontinuous. At about 1000 atmospheres pressure the curve merges again into the calculated curve where the value of K is only slightly higher than the average. It is evident from a glance at the graph that if the data extended above 1000 atmospheres pressure the K values would regain their former constancy.

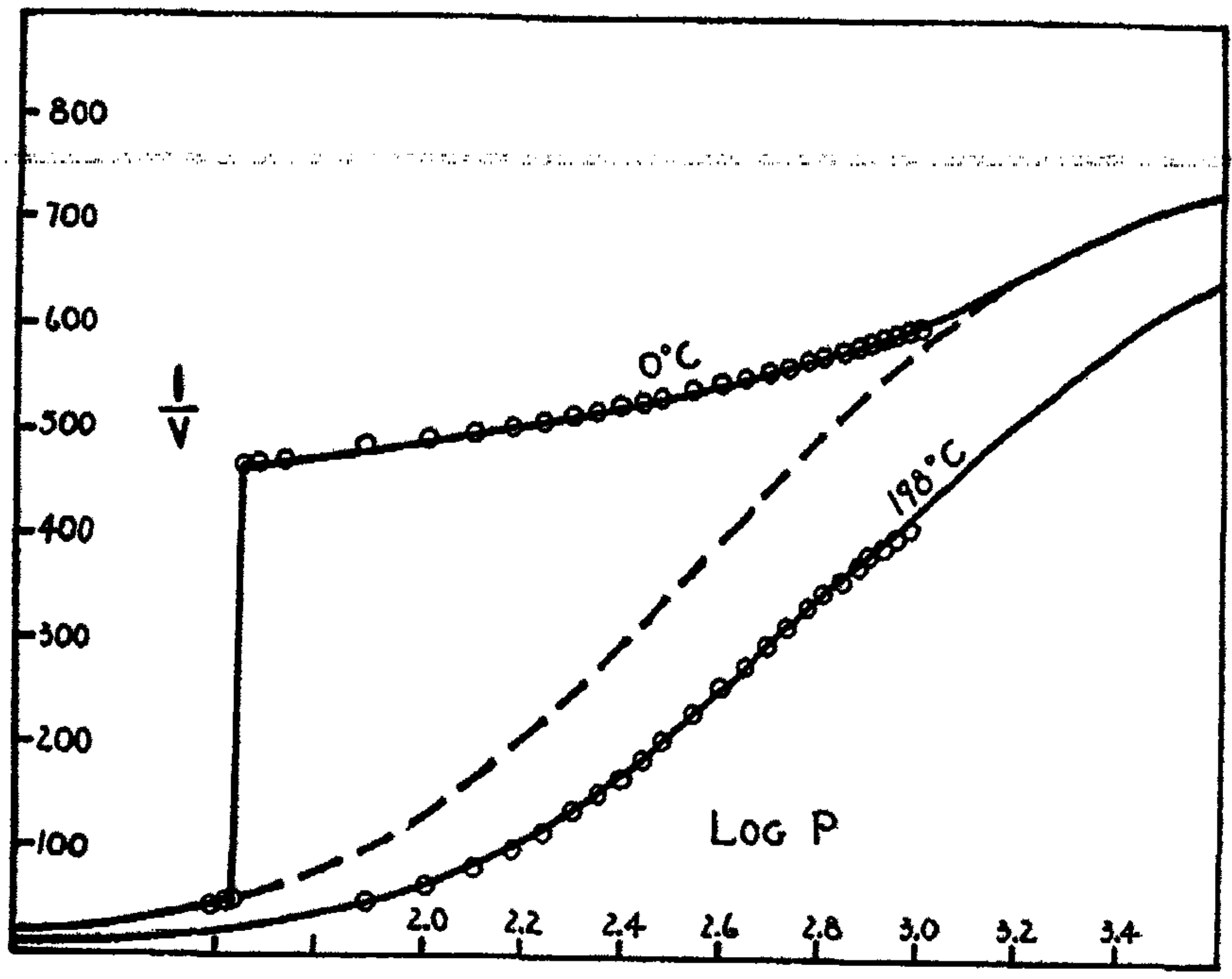

FIG. 2. P-V-T RELATIONS OF CARBON DIOXIDE GAS

To obtain a comparative view of the experimental deviations for the several gases, the values calculated for −50°C. and for +50°C. seem sufficient and representative. These are given in table 2. They were calculated from the equation,

$$(dC/C) = (C_\infty - C)/C_\infty(\log_e P)dK$$

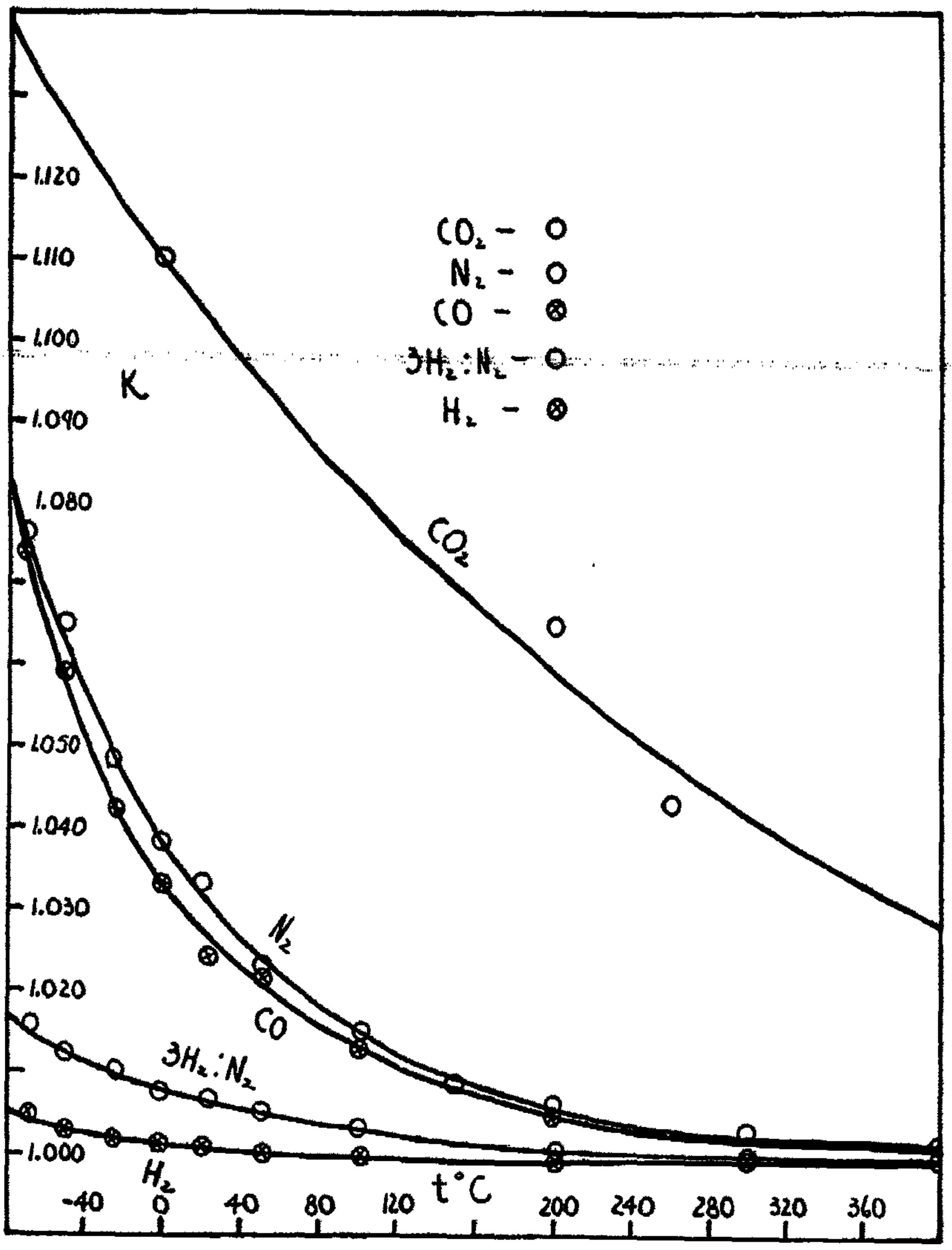

Fig. 3. Relation of K and t

where C denotes the molal density (since the quantity of gas is always 1 mole, $C = 1/V$) of the gas at pressure P; C_∞, the ultimate molal density at infinite pressure; and dK, the difference between any value for K and the arithmetic mean of a given series. The above equation is obtained by differentiating the original equation for a given pressure.

TABLE 1

Summary of the values of K

T	H_2		$3H_2:N_2$		N_2		CO		CO_2	
	K_m	K_r	K_m	K_r	K_m	K_r	K_m	K_r	K_m	K_r
degrees C.										
−70	1.004	1.002 1.006	1.015	1.012 1.020	1.076	1.049 1.102	1.073	1.031 1.110		
−50	1.003	1.001 1.004	1.012	1.005 1.016	1.065	1.042 1.079	1.060	1.022 1.083		
−25	1.002	1.001 1.003	1.101	1.004 1.012	1.048	1.035 1.060	1.042	1.015 1.060		
0	1.001	1.001 1.002	1.008	1.004 1.009	1.038	1.024 1.048	1.033	1.013 1.048	1.110	1.104 1.112
20	1.001	1.001 1.001			1.033	1.026 1.040				
25			1.007	1.003 1.008			1.024	1.010 1.038		
50	1.000	1.000 1.000	1.005	1.002 1.005	1.023	1.012 1.030	1.022	1.008 1.031		
100	1.000	1.000 1.000	1.004	1.002 1.004	1.015	1.007 1.020	1.013	1.005 1.020		
150							1.008	1.001 1.012		
200	1.000	0.999 1.000	1.001	1.000 1.001	1.006	1.002 1.008	1.005	1.000 1.008	1.065	1.029 1.081
300	1.000	0.999 1.000	1.000	1.000 1.000	1.003	1.002 1.004				
400	1.000	1.000 0.999			1.001	1.000 1.001				

All the deviations are calculated on the basis of four significant figures in the corresponding values for K, since 0.1 per cent variation in K is within the probable experimental error mentioned in the original articles cited above.

In conclusion it may be pointed out that the most concordant data are those of hydrogen gas by Bartlett, and the least concordant data are those for carbon dioxide gas by Amagat.

EXPLANATION OF THE TABLES

In table 1 is given a summary of the constants, where K_m denotes the arithmetic mean at a given temperature over the pressure range shown in column 1, table 2. Under K_r are given the largest and the smallest K values, or the range, of a given series. The other headings are self-explanatory. In table 2 are given the calculated deviations and the values for V_∞ of the several gases. The averages at the foot of table 2 were calculated without regard to the algebraic signs prefixed to the individual deviations. The values for the ultimate molal volumes are placed at the conclusion of table 2. The values for V_1, the molal volumes at 1 atmosphere pressure, may be found at the head of the columns marked PV in Bartlett's (2) original tables.

TABLE 2

Values of (dC/C)

P	H_2		$3H_2:N_2$		N_2		CO		CO_2
	−50°C.	+50°C.	−50°C.	+50°C.	−50°C.	+50°C.	−50°C.	+50°C.	+198°C.
atmospheres									
25	+0.0063		+0.0220				+0.1053	+0.0349	
50	+0.0037	0.0000	+0.0186	+0.0113		+0.0409	+0.0649	+0.0297	
75	0.0000		+0.0120				+0.0114	+0.0160	
100	0.0000	0.0000	+0.0081	+0.0086	+0.0192	+0.0124	−0.0346	+0.0041	+0.0912
125	0.0000		0.0000		−0.0114		−0.0612	−0.0085	+0.0524
150	−0.0044		−0.0043		−0.0489		−0.0830	−0.0171	+0.0398
200	−0.0045	0.0000	−0.0130	+0.0046	−0.0506	−0.0170	−0.0985	−0.0300	0.0000
300	−0.0045	0.0000	−0.0170	0.0000	−0.0432	−0.0290	−0.0710	−0.0375	−0.0584
400	−0.0088	0.0000	−0.0164	0.0000	−0.0402	−0.0279	−0.0350	−0.0322	−0.0637
500	−0.0043		−0.0119		−0.0058		−0.0415	−0.0194	−0.0489
600	−0.0041	0.0000	−0.0076	0.0000	+0.0220	−0.0146	+0.0232	−0.0112	−0.0295
800	0.0000	0.0000	−0.0035	0.0000	+0.0373	+0.0034	+0.0564	+0.0174	+0.0236
1000	0.0000	0.0000	0.0000	0.0000	+0.0520	+0.0094	+0.0749	+0.0294	
Av..	0.0031	0.0000	0.0103	0.0031	0.0330	0.0193	0.0585	0.0230	0.0464
V_∞..	0.0007200		0.0008525		0.001250		0.001025		0.001250

SUMMARY

In this paper additional calculations are presented showing the P-V-T relations of single and composite gases over the widest temperature and pressure ranges thus far investigated. The *P–V–T* relations are interpreted with the aid of a simple algebraic expression of one constant which increases with the increase in the molecular weight of the gas, but which approaches unity with increase in temperature for all the gases and their mixtures thus far studied. This phenomenon is illustrated arithmetically in table 1 and graphically in figure 3 of this article and in figure 5 of the previous article.

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KINETICS OF THE FORMATION OF SULFONIC ACIDS FROM DITHIO ACIDS. I

The Oxidation of Cystine to Cysteic Acid by Thallic Sulfate[1]

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Received February 23, 1934

The mechanism of the oxidation and reduction reactions of sulfur compounds of the type R—S—S—R and R—SH is of interest because of the peculiar chemical reactions of these substances, their widespread occurrence in biological materials, and their supposed participation in the oxidation and reduction systems of the living organism.

When R—SH and R—S—S—R compounds are treated with sufficiently powerful oxidizing agents, the end product, if the organic radical is not attacked, usually is the corresponding sulfonic acid, $R{-}SO_3H$. The direct oxidation pathway might be represented as follows:

$$2(R{-}SH) \xrightarrow{-2H} R{-}S{-}S{-}R \xrightarrow{+O + H_2O} 2(R{-}SOH) \xrightarrow{+O} (R{-}SO_2H) \xrightarrow{+O} R{-}SO_3H$$

The existence of the intermediates, R—SOH and $R{-}SO_2H$ or their derivatives, for this series has not been demonstrated by stepwise oxidation of such sulfur compounds in aqueous solutions.

Recent investigations of the reactions of metallic salts with R—S—S—R demonstrate the formation of $R{-}SO_3H$ and R—SH according to the following equation

$$3R{-}S{-}S{-}R + 3H_2O = 5R{-}SH + R{-}SO_3H$$

This reaction appears to be an intramolecular oxidation-reduction driven by the removal of R—SH in the following series of hypothetical equilibria:

$$R{-}S{-}S{-}R + H_2O \rightleftarrows R{-}SH + R{-}SOH$$
$$R{-}SOH + H_2O + R{-}S{-}S{-}R \rightleftarrows 2R{-}SH + R{-}SO_2H$$
$$R{-}SO_2H + H_2O + R{-}S{-}S{-}R \rightleftarrows 2R{-}SH + R{-}SO_3H$$

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[1] This research was aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

This paper was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the meeting held in Washington, D. C., March, 1933.

The R—SH may be removed by precipitation as a silver salt by Ag^+ (6, 10), or as a mercuric salt by Hg^{++} (2, 9), through formation of an unionized complex by mercuric halide ions $BrHg^+$ (7), or through a combination oxidation and precipitation as a cuprous salt by Cu^{++} (8). If the R—SH formed in the above reaction with water is not removed but instead is reoxidized to R—S—S—R, there would be a continuous accumulation of $R—SO_3H$, which would ultimately appear as a complete conversion of R—S—S—R into $R—SO_3H$.

Since the possibility of isolating and identifying certain of the intermediates seems remote, an attempt has been made to obtain information concerning the mechanism of the reaction by kinetic measurements of the oxidation of R—S—S—R to $R—SO_3H$ by various oxidizing agents.

The oxidation of cystine, $HOOC \cdot CHNH_2 \cdot CH_2S \cdot SCH_2 \cdot CHNH_2 \cdot COOH$, by thallic sulfate was selected, because with this oxidizing agent the reaction proceeds essentially quantitatively to cysteic acid, $HOOC \cdot CHNH_2 \cdot CH_2SO_3H$ and thallous sulfate. Thallic sulfate, further, forms with thallous sulfate a reversible oxidation-reduction system of known potential or oxidizing intensity, so that the results obtained may be useful for comparison with the data being obtained for other reversible oxidation-reduction systems.

EXPERIMENTAL

Preparation of reagents

Since chloride, bromide, and iodide were found to have unusual catalytic effects upon the reaction, special care was exercised in the selection of materials and preparation of solutions to insure that these substances would not be present in significant quantities.

Thallic oxide was suspended in 2.000 *N* sulfuric acid and dissolved by warming and concentrating to about 4 *N*. After proper dilution, the final solution was 0.005 gram-atomic in thallic sulfate and 1.000 *N* in sulfuric acid.

Cystine was prepared by the customary hydrochloric acid hydrolysis of hair and purified by several precipitations from sulfuric acid solution by sodium carbonate. The purity was checked by nitrogen determinations made by West and Brandon (11). The final solution was 0.01 *M* in cystine and 1.000 *N* in sulfuric acid.

Experimental procedures

The required amounts of sulfuric acid, water, and thallic sulfate were measured into a 250-cc. wide-mouth Pyrex flask which was immersed in a thermostat maintained within 0.1°C. At zero time the cystine solution was pipetted into the flask, which was shaken rapidly.

The reaction was stopped by suddenly adding 1 g. of potassium iodide in

25 cc. of water. The excess thallic salt was determined by adding freshly prepared starch as indicator, and immediately titrating with 0.01 *N* sodium thiosulfate, drop by drop, in diffuse or artificial light. The color change was from a greenish blue, through yellowish green, to the final bright yellow suspension of precipitated thallous iodide. Before again using the reaction flasks, they were thoroughly cleaned with chromic-sulfuric acid mixture. Ten such experiments with different time intervals determined the reaction rate constant for the particular conditions.

Determination of the products of the reaction

Several typical experiments were made with 60 cc. of 0.005 gram-atomic thallic sulfate solution reacting with 5 cc. of 0.01 *M* cystine solution at 30°C. The amount of thallic salt reduced (see table 1) approaches a maximum of 10 oxidation-reduction equivalents per mole of cystine, which suggests the equation

$$\begin{gathered}2\mathrm{HOOC{\cdot}CHNH_2{\cdot}CH_2S{\cdot}SCH_2{\cdot}CHNH_2{\cdot}COOH} + 5\mathrm{Tl_2(SO_4)_3} + 12\mathrm{H_2O} = \\ 4\mathrm{HOOC{\cdot}CHNH_2{\cdot}CH_2SO_3H} + 5\mathrm{Tl_2SO_4} + 10\mathrm{H_2SO_4}\end{gathered}$$

Experiments with the related dithiodihydracrylic acid, $\mathrm{HOOC{\cdot}CH_2{\cdot}CH_2S{\cdot}SCH_2{\cdot}COOH}$, gave further indication that R—S—S—R type acids are oxidized almost entirely to $\mathrm{R{-}SO_3H}$ acids. Mixtures of 0.07317 g. of this acid as the disodium salt and 20 cc. of 0.174 *N* thallic perchlorate in *N* perchloric acid were allowed to react for 40 hours at 37°C. The $\mathrm{Ba({\cdot}OOC{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3{\cdot})}$ formed was isolated and analyzed according to a modification of the procedure previously reported (6). The $\mathrm{R{-}SO_3H}$ yield was 99 per cent of the theoretical and all except a trace of thallic salt was reduced (see table 2).

RESULTS OF KINETIC EXPERIMENTS

Mathematical considerations

The equation of the reaction indicates that 5 gram-atoms of thallic are reduced as 1 mole of cystine is oxidized. To permit the use of the less complex equations applying to pseudo first-order reactions, the cystine concentration was always made sufficiently high so that its initial concentration would change less than 10 per cent during the period of measurement. In calculating the reaction rate constants, only values between 20 and 80 per cent complete reaction were included and the arithmetical average of ten determinations, nearly equally spaced with respect to time, within this range, was considered sufficiently representative of the reaction rate under the particular conditions of the experiment. With but very few exceptions, the maximum variation of the constant in a particular series of ten values is less than 10 per cent. Table 3 gives the results of a typical series of determinations.

TABLE 1

Determination of the maximum number of reducing equivalents of cystine towards thallic sulfate

MINUTES AT 30°C.	EQUIVALENTS OF THALLIC SULFATE PER MOLE OF CYSTINE	MINUTES AT 25°C.	EQUIVALENTS OF THALLIC SULFATE PER MOLE OF CYSTINE
30	4.652	840	9.800
60	6.464	840	9.900
120	8.142	2400	9.980
180	8.720	2400	10.002
240	9.242		
300	9.406		
480	9.780		
840	9.876		
1240	9.994		
1470	10.012		

TABLE 2

Quantity of sulfonic acid produced from dithiodihydracrylic acid by thallic sulfate

$Ba(\cdot OOC\cdot CH_2\cdot CH_2\cdot SO_3\cdot)$ ISOLATED	PER CENT Ba
grams	
0.1982	47.0
0.2010	47.0
0.1992	47.0
0.1979	47.2
0.1995	47.1
Av. = 0.1992	47.1
Theor. = 0.2015	47.4

TABLE 3

The results of a typical series of determinations

Temperature, 30°C.; thallic sulfate concentration 0.0005 gram-atomic; sulfuric acid concentration, 0.5 *N*; cystine concentration, 0.002 *M*

MINUTES	FRACTION OF THALLIC REDUCED	*k* (PSEUDO FIRST ORDER)
3	0.263	0.102
4	0.330	0.100
5	0.418	0.108
6	0.453	0.101
7	0.524	0.106
8.5	0.589	0.105
10	0.650	0.105
12	0.717	0.105
14	0.761	0.102
16	0.800	0.101
Average		0.104

From the pseudo first-order constant calculated from the disappearance of thallic salt, the second-order constant may be calculated by dividing by the concentration of cystine. The value so obtained represents the rate at which the thallic salt was being reduced, calculating on a gram-atomic thallic and a molar cystine basis; the rate of cystine oxidation is only one-fifth of this rate.

The results are summarized in tables 4 through 8. Each experiment numbered x is the same as some experiment listed in another table which has been inserted twice to preserve unity. Experiments lettered are inserted to show special effects of changing several variables.

TABLE 4

Effect of the concentration of the reactant, thallic sulfate, upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
1	0.001	0.000125	1.0	0.0151	15.1
2	0.001	0.0001875	1.0	0.0177	17.7
3	0.001	0.00025	1.0	0.0197	19.7
4	0.001	0.000375	1.0	0.0220	22.0
5	0.001	0.0005	1.0	0.0234	23.4
6	0.001	0.001	1.0	0.0233	23.3
7	0.001	0.002	1.0	0.0227	22.7
A	0.001	0.00025	0.5	0.0478	47.8
Bx	0.001	0.0005	0.5	0.0547	54.7
C	0.001	0.001	0.5	0.0564	56.4

Thallic concentration effects

The values of *K* increase with an increase in thallic concentration until 0.0005 gram-atomic is reached; then nearly constant values are attained, showing that the reaction rate is probably proportional to the thallic concentration.

The oxidation-reduction potential values show similar changes (1), becoming less oxidizing as the thallic concentration is decreased below 0.0005 gram-atomic while keeping the thallic–thallous ratio the same. Whether the potential and rate changes are related remains for further work to decide.

Cystine concentration effects

As the concentration of cystine is increased there is a slight decrease in *K* (see table 5). At values above 0.002 molar, *K* becomes nearly constant, so that the reaction rate may be considered proportional to the cystine concentration.

TABLE 5

Effect of the concentration of the reactant, cystine, upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
11	0.0005	0.0005	1.0	0.0123	24.6
12	0.00075	0.0005	1.0	0.0169	22.7
13x	0.001	0.0005	1.0	0.0234	23.4
14	0.002	0.0005	1.0	0.0420	21.0
15	0.003	0.0005	1.0	0.0600	20.0
16	0.004	0.0005	1.0	0.0791	19.8
17	0.005	0.0005	1.0	0.097	19.4
21x	0.001	0.001	1.0	0.0233	23.3
22	0.002	0.001	1.0	0.0422	21.1
23	0.003	0.001	1.0	0.0625	20.8
24	0.004	0.001	1.0	0.0807	20.2
25	0.005	0.001	1.0	0.103	20.6
D	0.0005	0.0005	0.5	0.0294	68.8
Ex	0.001	0.0005	0.5	0.0547	54.7
F	0.002	0.0005	0.5	0.104	52.0

TABLE 6

Effect of the concentration of the product, thallous sulfate, upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS				K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	Tl_2SO_4	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-atoms* Tl	*gram-equivalents*		
31	0.001	0.0005	0.0025	1.0	0.0237	23.7
31x	0.001	0.0005		1.0	0.0234	23.4
32	0.001	0.00025	0.0025	1.0	0.0204	20.4
32x	0.001	0.00025		1.0	0.0197	19.7
33	0.001	0.000375	0.001875	1.0	0.0233	23.3
33x	0.001	0.000375		1.0	0.0220	22.0
34	0.001	0.0005	0.005	0.5	0.0552	55.2
34x	0.001	0.0005		0.5	0.0547	54.7

Thallous sulfate concentration effects

The lack of significant change in the ten pseudo first-order constants obtained in a particular experiment and the close agreement between the values of K (see table 6) for experiments with and without initially added thallous, indicate that thallous concentration and consequently also the oxidation-reduction potential of the thallic–thallous system have no apparent effect on the reaction rate.

TABLE 7

Effect of the concentration of sulfuric acid upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
41	0.001	0.0005	0.25	0.143	143.0
42	0.001	0.0005	0.375	0.0918	91.8
44	0.001	0.0005	0.5	0.0547	54.7
44	0.001	0.0005	0.75	0.0335	33.5
45	0.001	0.0005	1.0	0.0238	23.8
46	0.001	0.0005	1.25	0.0163	16.3
47	0.001	0.0005	1.5	0.0135	13.5
48	0.001	0.0005	1.8	0.0113	11.3

TABLE 8

Effect of temperature on the rate of reaction at different acidities

EXPERIMENT NO.	TEMPERATURE	INITIAL CONCENTRATION			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
		Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	degrees C.	*gram-moles*	*gram-atoms* Tl	*gram-equivalents*		
1 T	15	0.001	0.0005	0.25	0.0171	17.1
2 T	15	0.001	0.0005	0.5	0.00720	7.20
3 T	20	0.001	0.0005	0.25	0.0319	31.9
4 T	20	0.001	0.0005	0.5	0.0137	13.7
5 T	20	0.001	0.0005	1.0	0.00587	5.87
6 T	25	0.001	0.0005	0.25	0.0709	70.9
7 T	25	0.001	0.0005	0.5	0.0287	28.7
8 T	25	0.001	0.0005	1.0	0.0117	11.7
9 Tx	30	0.001	0.0005	0.25	0.143	143.0
10 Tx	30	0.001	0.0005	0.5	0.0547	54.7
11 Tx	30	0.001	0.0005	1.0	0.0238	23.8
12 T	35	0.001	0.0005	0.5	0.100	100.0
13 T	35	0.001	0.0005	1.0	0.0404	40.4

Sulfuric acid concentration effect

The reaction rate decreases with an increase in sulfuric acid concentration (see table 7). No simple relation could be found between the rate and several of the usual methods of expressing acidities, and considering that cystine has two acidic and two basic ionizations in or near the region of acidity used, this is not surprising.

Temperature effects

The reaction rates at three acidities were determined (see table 8), and the graph of the reciprocal of the absolute temperature plotted against the logarithm of K results in three parallel lines whose slope is such that $Q = 24{,}200$ calories in the Arrhenius equation (3).

DISCUSSION AND SUMMARY

The kinetic experiments performed indicate that the rate-controlling step in the measured reaction between thallic sulfate and cystine in sulfuric acid solution is a second-order reaction.

The rate of reaction is approximately proportional to the cystine concentration and the thallic sulfate concentration and decreases with an increase in the sulfuric acid concentration. The equation for the complete reaction is

$$\begin{gathered}2HOOC\cdot CHNH_2\cdot CH_2S\cdot SCH_2\cdot CHNH_2\cdot COOH + 5Tl_2(SO_4)_3 + 12H_2O = \\ 4HOOC\cdot CHNH_2\cdot CH_2SO_3H + 5Tl_2SO_4 + 10H_2SO_4\end{gathered}$$

and indicates that 5 gram-atoms of thallic are reduced as 1 gram-mole of cystine is oxidized. At 30°C. in 1 N sulfuric acid with 0.0005 gram-atomic thallic sulfate and 0.001 M cystine, the value of the second-order constant for thallic reduction is $K_{\mathrm{Tl}} = 23.3$ gram-atoms per minute per liter; for cystine oxidation under the same conditions $K_{\mathrm{Cys.}} = 4.7$ moles per minute per liter.

Since several second-order reactions are possible in the series leading from R—S—S—R to R—SO$_3$H, the identification of a particular reaction is not possible with the data at hand. However, two reactions can be eliminated as being involved in the rate-controlling step with thallic salt as oxidant: the reaction of R—S—S—R with H$_2$O to give R—SH and R—SOH, since this would result in the reaction being independent of the concentration of the thallic salt; and the oxidation by thallic salt of R—SH formed by hydrolysis, since this oxidation would probably not be a simple bimolecular reaction. The approximate constancy of $K_{\text{pseudo first order}}$ in a particular series and the lack of an appreciable effect upon the rate of reaction upon the addition of thallous salt practically eliminates the possibility that the rate-controlling step involves a labile, reversible, electromotively active oxidation-reduction system (4, 5) composed of intermediate oxidation stages of the sulfur compounds.

The energy of activation, Q, was found to be 24,200 calories at various acidities.

The oxidation of R—S—S—R to $R—SO_3H$ by various oxidizing agents is being studied in the hope of solving the problem of the mechanism of this complex oxidation.

The authors are indebted to Dr. P. A. Shaffer for his many helpful suggestions and his constant interest in the work.

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KINETICS OF THE FORMATION OF SULFONIC ACIDS FROM DITHIO ACIDS. II

THE POSITIVE AND NEGATIVE CATALYTIC EFFECTS OF HALIDES UPON THE OXIDATION OF CYSTINE TO CYSTEIC ACID BY THALLIC SULFATE[1]

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Received February 23, 1934

During the oxidation of cystine (R—S—S—R—) to cysteic acid (R—SO_3H) by thallic sulfate (1), it was found that whereas high concentrations of iodide could be used to inhibit or stop the reaction, lower concentrations caused great acceleration of the rate of reaction. An investigation of this interesting and unusual effect of iodide and the effects of the other halides has been made to obtain additional information on the mechanism of the oxidation of R—S—S—R to R—SO_3H.

CATALYSIS AND INHIBITION BY IODIDE

The final result of the reaction between cystine and thallic sulfate can be represented (1) by the equation,

$$2HOOC{\cdot}CHNH_2{\cdot}CH_2S{\cdot}SCH_2{\cdot}CHNH_2{\cdot}COOH + 5Tl_2(SO_4)_3 + 12H_2O = 4HOOC{\cdot}CHNH_2{\cdot}CH_2SO_3H + 5Tl_2SO_4 + 10H_2SO_4$$

which apparently holds also for the iodide catalysis. A series of experiments was performed in which 60 cc. of 0.005 gram-atomic thallic sulfate in *N* sulfuric acid and 10 cc. of 0.001 *M* potassium iodide were allowed to react for 1 minute at 27°C. and then 5 cc. of 0.01 *M* cystine in 1 *N* sulfuric acid was added. The amount of thallic reduced was as follows:

Time (in minutes)	0.5	1	2	5	20	90
Reduction (in equivalents per mole of cystine)	8.036	9.900	9.896	9.880	9.984	9.960

The procedure used in the experiments which follow was identical with that used in the preceding paper. The halide solutions were made from

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[1] This research was aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

This paper was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the meeting held in Washington, D. C., March, 1933.

samples selected for their high purity and absence of significant quantities of the other halides.

Effect of iodide concentration

When the potassium iodide, thallic sulfate, and sulfuric acid were mixed and allowed to interact for various periods of time, and then the cystine was added and allowed to react for a particular period of time, the amount of thallic reduced was found to decrease slightly with an increase in the first time period. This same result was obtained when the reaction took place under nitrogen. When cystine, potassium iodide, and sulfuric acid were mixed and allowed to stand for varying time periods and then thallic added, no difference in the amount of reduction was noted. The latter procedure was adopted, although the retarding effect cannot be eliminated completely even in this manner, since the iodide thallic reaction undoubtedly proceeds simultaneously with the positive catalytic reaction; however, when the total reaction time is short, the error thus introduced is small.

TABLE 1

Calculation of a typical experiment

Reaction mixture: 0.0005 gram-atomic $Tl_2(SO_4)_3$, 0.001 *M* cystine, 1.0 *N* H_2SO_4, and 0.000,002 *M* KI. Temperature, 30°C.

TIME	FRACTION PRESENT AT BEGINNING OF THE MINUTE PERIOD	TOTAL FRACTION REDUCED	FRACTION OF UNCATALYZED REACTION IN PAST MINUTE	TOTAL UNCATALYZED REACTION	TOTAL KI-CATALYZED REACTION
minutes					
0	1.000				
1	0.799	0.201	0.022	0.022	0.179
2	0.612	0.388	0.018	0.040	0.348
3	0.442	0.558	0.013	0.053	0.505
4	0.286	0.714	0.010	0.063	0.651
5	0.100	0.900	0.006	0.069	0.831

The amount of reaction due to the catalytic effect was determined by correcting the experimental values for the normal uncatalyzed reaction going on at the same time (1). As an example, the corrections made on the reaction with 0.000,002 *M* potassium iodide and 0.0005 gram-atomic thallic sulfate are given.

The fraction of the total reaction which took place in 1 minute was calculated. Then the appropriate fraction of the normal reaction taking place in the preceding time was subtracted from each experimental value. (See table 1).

The values of $K_{\text{catalytic}}$ listed in table 2 are the arithmetic means of the values obtained for 1-minute intervals in the series. They represent the number of oxidizing equivalents of thallic reduced (at the concentrations specified) per liter per minute per mole of iodide initially present.

The positive catalytic effect of iodide first becomes noticeable at 0.000,000,1 *M* potassium iodide and increases until a maximum is reached at about 0.000,05 *M*, after which the effect diminishes, and at 0.01 *M* and higher the rate becomes even less than when iodide is absent (see table 2).

Effect of thallic sulfate concentration

The catalysis depends also upon the ratio of the initial iodide to initial thallic concentrations (see table 2). For the three experiments where $(I^-)/(Tl^{+++}) = 0.002$, the fractions of thallic reduced in a given time through catalysis are essentially the same. Similar relationships hold also for certain other ratios.

When the ratio is changed by varying the initial iodide concentration, the rate of catalytic reduction increases as the ratio is increased. For the higher accelerating concentrations, the effect of the initial thallic concentration becomes less pronounced and the rate is only slightly increased as the ratio is increased and appears to be proportional to iodide alone.

During a particular series of experiments, the ratio of $(I^-)/(Tl^{+++})$ increases with an increase in time, because of the reduction of the thallic to thallous. The catalytic rate remains almost constant. These results might be explained on the assumption that the thallic reacts very rapidly with iodide to form a quantity of unreactive, slowly dissociating complexes, thereby preventing some of the iodide from taking part in the catalytic reaction.

Effect of cystine or thallous sulfate concentration

Cystine or thallous sulfate concentration changes do not alter the catalytic reduction rate.

Effect of sulfuric acid concentration

Increases in the sulfuric acid concentration cause the catalytic reaction rate to decrease. For a mixture of 0.0005 gram-atomic thallic, 0.001 *M* cystine, and 0.000,001 *M* iodide at 30°C., the difference in rate at 0.5 *N* and 1.5 *N* acid is about 40 per cent.

Effect of temperature

The effect of temperature on iodide catalysis was determined by a group of experiments at 0.0005 gram-atomic thallic, 0.001 *M* cystine, in *N* acid with various initial iodide concentrations and temperatures (see table 3). The temperature coefficient, Q, is 21,700 calories for that part of the reaction apparently proceeding through iodide catalysis. For the uncatalyzed reaction $Q = 24{,}200$ calories (1).

TABLE 2

Effect of iodide and thallic concentrations

KI	$Tl_2(SO_4)_3$	$\frac{(I)}{(Tl^{III})}$	K (CATALYTIC) AVERAGE	TIME IN MINUTES																
				0.5	1.0	1.5	2	3	4	5	6	7	8	9	10	15	20	25	30	40
moles per liter	*gram-atoms per liter*															Fraction $Tl_2(SO_4)_3$ reduced				
0.0	0.000,125	0.000														0.214	0.268	0.307	0.353	
	0.000,25															0.245	0.318	0.370	0.422	0.558
	0.000,5														0.197	0.280	0.341	0.412	0.471	0.576
	0.001														0.210	0.300	0.374	0.425	0.499	0.610
				Fraction $Tl_2(SO_4)_3$ reduced (total) *Fraction $Tl_2(SO_4)_3$ reduced through iodide (calculated)*																
0.000,000,1	0.000,5	0.0002													0.228 *0.034*	0.327 *0.053*	0.405 *0.062*	0.481 *0.077*	0.539 *0.082*	0.651 *0.106*
0.000,000,5	0.000,125	0.004	(103,500)		0.239 *0.224*		0.451 *0.425*	0.645 *0.611*												
	0.000,25	0.002	78,000				0.203 *0.167*	0.291 *0.240*	0.372 *0.308*	0.480 *0.404*	0.552 *0.466*	0.649 *0.554*	0.746 *0.644*	0.816 *0.709*	0.903 *0.792*					
	0.000,5	0.001	62,000						0.228 *0.142*	0.274 *0.171*	0.322 *0.230*	0.376 *0.242*	0.421 *0.273*	0.469 *0.308*	0.502 *0.329*	0.708 *0.482*	0.908 *0.650*			
0.000,001	0.000,25	0.004	85,000		0.186 *0.167*		0.383 *0.349*	0.553 *0.507*	0.743 *0.689*											
	0.000,5	0.002	79,000				0.221 *0.177*	0.316 *0.255*	0.392 *0.316*	0.492 *0.403*	0.575 *0.475*	0.670 *0.561*	0.757 *0.641*	0.842 *0.721*	0.930 *0.806*					

	0.001	0.001	64,000						0.242 *0.156*	0.283 *0.180*	0.328 *0.209*	0.379 *0.245*	0.430 *0.282*	0.469 *0.308*	0.518 *0.345*	0.715 *0.490*	0.901 *0.646*		
0.000,002	0.000,5	0.004	83,000		0.201 *0.179*		0.388 *0.348*	0.558 *0.505*	0.714 *0.651*	0.900 *0.831*									
	0.001	0.002	77,000				0.233 *0.189*	0.327 *0.266*	0.412 *0.336*	0.502 *0.413*	0.589 *0.489*	0.665 *0.556*	0.750 *0.634*	0.837 *0.716*					
0.000,005	0.000,5	0.01	92,000	0.260 *0.249*	0.489 *0.470*	0.730 *0.705*	0.950 *0.922*												
0.000,01	0.000,5	0.02	(97,800)	0.500 *0.489*															
0.000,01	0.001	0.01	87,800	0.279 *0.268*	0.481 *0.462*	0.694 *0.669*	0.906 *0.878*												
0.000,05	0.000,5	0.1		(1.00)															
0.000,1	0.000,5	0.2		(0.91)															
0.000,5	0.000,5	1.0		(0.64)															
0.001	0.000,5	2.0		(0.53)															
0.01	0.000,5	20.0		0.003	0.000														

EFFECTS OF CHLORIDE, BROMIDE, AND FLUORIDE

The results obtained with chloride or bromide under conditions similar to those used with iodide may be briefly summarized. Essentially complete and immediate inhibition occurs when the halide–thallic ratio is 2 or greater. There is no appreciable accelerating effect. Fluoride shows neither a catalytic nor an inhibitory effect.

Rather unexpected is an enhanced acceleration induced by bromide, and to a lesser extent by chloride in the iodide-catalyzed reaction.

TABLE 3

Effect of temperature on iodide catalysis

IODIDE CONCENTRATION	TEMPERATURE t	TEMPERATURE T	$1/T$	AVERAGE K*	LOG$_{10}$ AVERAGE K*
moles	*degrees C.*	*degrees A.*			
0.000,000,5	35	308	0.3247	0.055	−1.2596
0.000,001	35	308	0.3247	0.138	−0.8601
0.000,000,5	30	303	0.3300	0.034	−1.4685
0.000,001	30	303	0.3300	0.081	−1.0915
0.000,002	30	303	0.3300	0.170	−0.7696
0.000,005	30	303	0.3300	0.475	−0.3233
0.000,000,5	25	298	0.3356	0.017	−1.7696
0.000,001	25	298	0.3356	0.044	−1.3565
0.000,002	25	298	0.3356	0.099	−1.0044
0.000,005	25	298	0.3356	0.265	−0.5768
0.000,001	20	293	0.3413	0.022	−1.6576
0.000,002	20	293	0.3413	0.053	−1.2757
0.000,005	20	293	0.3413	0.141	−0.8508
0.000,001	15	288	0.3472	0.012	−1.9208
0.000,002	15	288	0.3472	0.026	−1.5850
0.000,005	15	288	0.3472	0.076	−1.1192

* Equivalents of thallic reduced per liter per minute in a solution 0.0005 gram-atomic in thallic, 0.001 M in cystine, and 1.0 N in sulfuric acid.

DISCUSSION

The uncatalyzed reduction of thallic sulfate by cystine is a second-order reaction (1) and may be represented by $K = 23.3$ gram-atoms reduced (in a gram-atomic thallic solution molar in cystine and normal in sulfuric acid) per liter per minute. For the iodide-catalyzed reaction, K becomes somewhat greater as the initial iodide is increased and becomes less as the initial thallic is increased within certain ranges.

The value of $K_{\text{catalytic}}$ obtained by calculation as described on the basis of initial iodide approximates 80,000 to 100,000 oxidation-equivalents of thallic reduced per liter per minute per mole of initially added iodide for certain specific conditions.

The iodide catalysis appears to be a zero-order reaction over a wide range of concentrations, when proper allowance is made for the effect of thallic concentration on the initial iodide.

The inhibiting effects of chloride, bromide, and iodide are probably due to the formation of complex ions or groups with thallic. The conclusion is supported by the effects introduced by thallic changes and also by the lack of effect of fluoride, which has little tendency to form complexes with thallic.

The accelerating effect of the halides may be due to the liberation of a highly reactive form or compound of the halogen which may react more rapidly with cystine. A comparison of the oxidation-reduction potential of the thallic–thallous system to those of the halogen–halide systems reveals that thallic could liberate the halogens from halides. Bromine alone or in the presence of large amounts of bromide oxidizes cystine to cysteic acid at an immeasurably fast rate. Shinohara (2) has demonstrated that iodine also oxidizes cystine to cysteic acid, but at a relatively slow rate. This result makes it appear unlikely that the positive iodide catalysis proceeds through the formation of some iodide derivative ordinarily present in significant quantity in an acidified potassium iodide solution of iodine.

The study of these unusual catalyses is being continued with various R—S—S—R compounds and oxidizing agents.

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STUDIES ON OVERVOLTAGE. VII

Electrode Discharge Phenomena Studied by Means of an Electromagnetic Interrupter together with an Oscillograph[1]

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Received February 23, 1934

In previous articles (1) the authors have studied polarization phenomena by means of a commutator in connection with a potentiometer, also by means of a commutator in connection with an oscillograph (2).[2] Comparisons were made of the direct and commutator methods for measuring such phenomena. The results of all the earlier work indicate that both methods give identical values for electrode potentials when measurements are properly made. This is contrary to the findings of most other investigators in this field. It is generally stated that the commutator method gives lower values than the direct. The difference between the two is attributed to a part of the voltage measured by the direct method being used up in driving the current through some kind of a resistance other than electrolytic resistance at the surface of the electrode. This resistance is commonly referred to as "transfer resistance" or "surface resistance." The existence of such a resistance has been postulated for about one hundred years. If a surface resistance exists, then, of course, a part of the applied potential, which is the thing measured by the direct method, is used up as an *IR* drop at the electrode-solution interface, and, naturally, the electrodes themselves are not charged to so high a potential. The back potential, which is measured by the commutator method, must be less, therefore, than the value which the direct method gives by an amount equal to the *IR* drop through the film on the electrode. It is assumed, of course, that account is taken of the ordinary *IR* drop through the solution.

One of the most active supporters of the transfer resistance idea is E. Newbery. He has made about fifty thousand observations with the rotat-

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[1] The oscillograph used was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

[2] Since the publication of this article, our attention has been called to two articles by S. K. Waldorf in which he made use of an amplifier-oscillograph arrangement similar to ours in his study of dielectrics (Physics 3, 1 (1932); J. Franklin Inst. 213, 605 (1932)).

ing commutator and about two thousand with the cathode ray oscillograph during a period of about twenty years.

It was shown in earlier papers by the authors that most of the measurements made by a rotating commutator are averages and therefore practically valueless so far as furnishing information upon the question of transfer resistance is concerned.

Those who defend the transfer resistance idea base their support largely upon an instantaneous drop in electrode potential, almost universally observed, immediately after the polarizing circuit is opened. As Newbery states in a recent article (3), "We will first utilize these curves for a discussion of the nature and properties of the very controversial 'transfer resistance.' The most striking feature of each of these curves (he refers here to electrode discharge curves obtained with a cathode ray oscillograph) is the clear gap which appears between the upper and lower sections. The existence of this gap proves conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted. . . . . This resistance—transfer resistance—may be measured by observing the vertical height of the gap in the curves, calculating the corresponding change of E.M.F., and from this, calculating the resistance, the total current flowing being known. When this is done, it is found that although the gaps in the curves are wider at the higher current densities, the actual transfer resistances are lower. In fact, transfer resistance increases rapidly as the current density is lowered, and at very low current densities it is frequently above 100 ohms per sq. cm."

In an earlier article (2) the authors have presented results obtained with a rotating commutator in connection with a moving coil oscillograph that give no indication of an *IR* drop, except that due to the *IR* drop through the solution, when the charging circuit is suddenly opened.

The true nature of the drop in potential which takes place immediately after the polarizing circuit is opened could be determined much better if the curve representing such a drop could be superimposed upon another curve known to be due to an *IR* drop only; or on one known to be due to both an *IR* drop and the falling off of a true electrode potential. In the work to be described such an arrangement was used.

The desired result was accomplished by the substitution of an electromagnetic interrupter in place of the commutator. The circuits involved are represented in figure 1. The portion of the figure within the circle and labelled "Drum" represents the face of the rotating film drum. Supported in front of the drum are three pairs of bronze brushes, Br_1, Br_2, and Br_3. The pair of brushes Br_1 is short-circuited once during each revolution of the drum through the contact P_a. In a similar manner the pair Br_2 is short-circuited through P_b. The contacts P_a and P_b are permanently attached to the face of the drum, but contacts P_{c1}, P_{c2}, etc., are removable and only one is used at a time. The portion of the drum included in the angle φ is not covered by the film. When the Br_1 brushes are short-circuited the electromagnet A closes the circuit through the lamp L of the oscillograph. Just following this the brushes Br_3 are short-circuited through the contact P_c in some one of the positions 1, 2, 3, etc. This closes the circuit through the electromagnet C, which opens the polarizing circuit I_p. In this manner the start of the discharge interval can be located at any one of several points throughout the length of the film. After the entire length of the film has been exposed the lamp is turned off by means of the

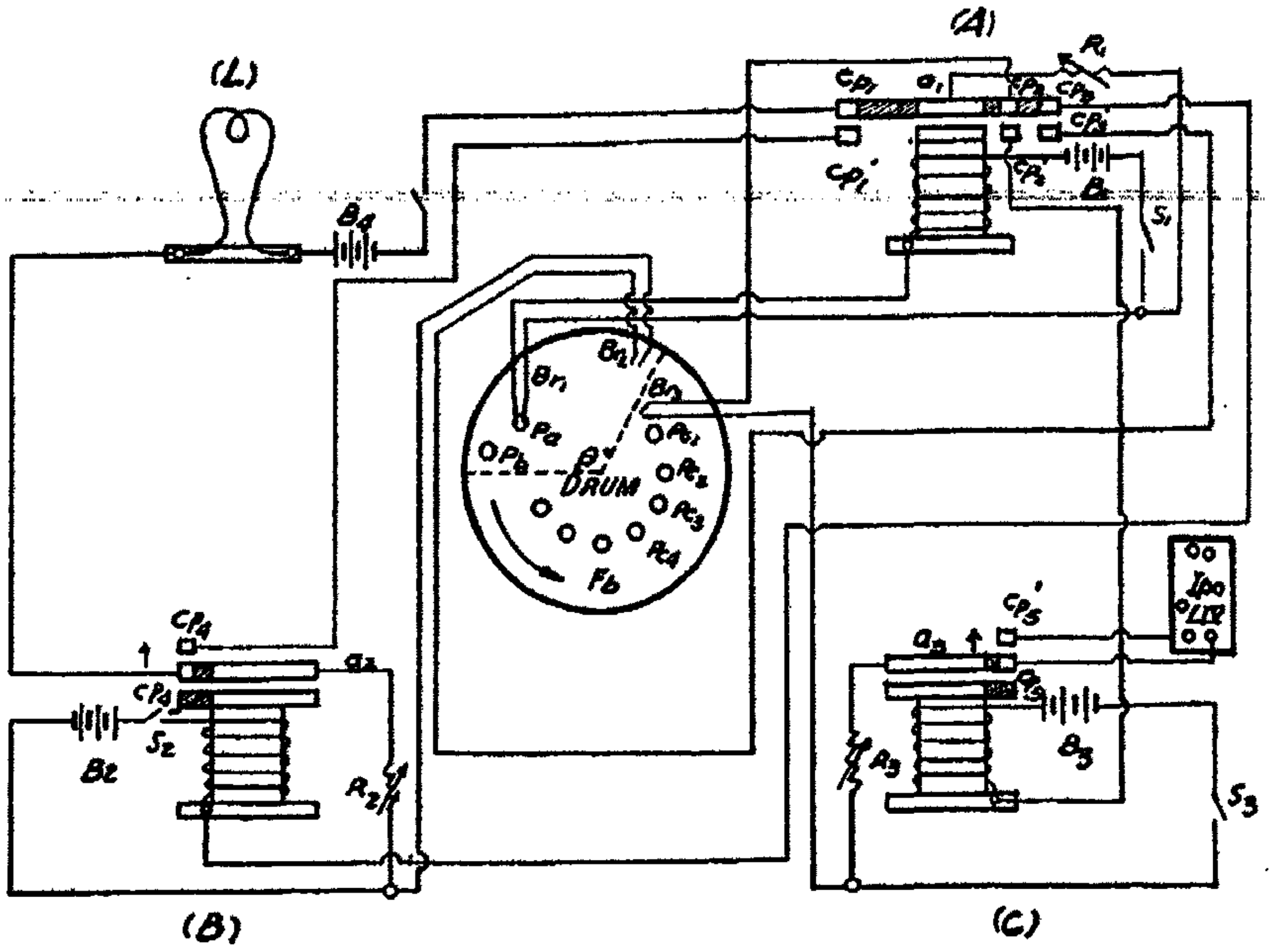

FIG. 1. CIRCUITS FOR ELECTROMAGNETIC INTERRUPTER

brushes Br_2 as they make contact at P_b, and thus the circuit through electromagnet B is closed.

As described in the previous article (2), the potential to be studied may first be measured with a potentiometer, which gives the value by the direct method; it is then applied to the grid circuit of the amplifier, and the voltage V_1 adjusted until the plate current as indicated by the ammeter is at some value near the upper part of the linear portion of the amplification curve. The plate current is then reduced to any desired value by the balancing potential V_2, so as to bring the line on any desired part of the width of the film. Although potentials of different magnitudes are applied to the grid circuit of the amplifier, it is possible by means of the variable voltages V_1 and V_2 to cause the same current to pass through the oscillograph. Under such conditions the lines on the film which correspond to the various potentials are superimposed up to the point where the polarizing current is interrupted, and, if the contact P_0 is in the same position on the drum face, each potential will be interrupted at the same point. The relative natures of the various discharging potentials may thus be directly determined.

In order to make a comparison between an *IR* drop and depolarization, pictures were taken of three types of potentials: (1) single electrode potential against its own reference electrode, which is either a pure potential or a pure potential plus a potential over transfer resistance; (2) single electrode potential against the opposite reference electrode, which is a pure potential plus the *IR* drop through the solution and plus an *IR* drop due to transfer resistance, if any exists; (3) the potential between the reference electrodes, which is due only to the *IR* drop through the solution and any transfer resistances at the electrode surfaces. The same electrolysis system was used as described in a previous paper; the electrodes were platinized platinum and the solution 2 *N* sulfuric acid.

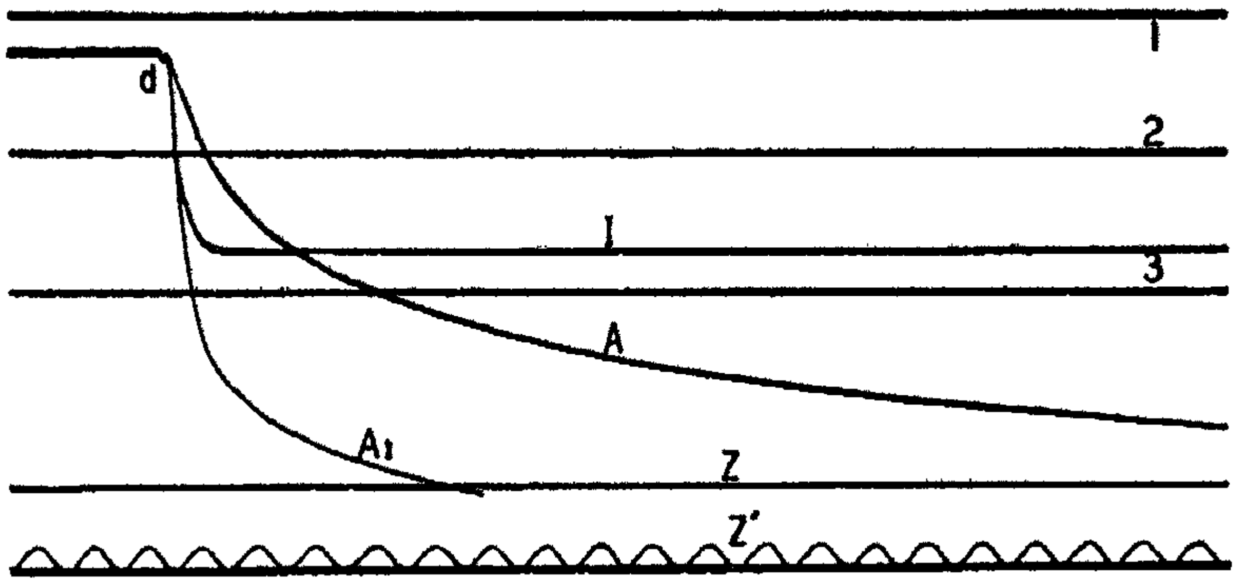

FIG. 2. DISCHARGE CURVES OF VARIOUS TYPES

A = potential of anode against anode standard; A_I = potential of anode against cathode standard; *I* = potential of anode standard against cathode standard.

In figure 2 are three curves: *A* shows the drop in potential of the anode as measured against the anode standard; A_I shows the drop in potential of the anode as measured against the cathode standard, and includes, therefore, the *IR* drop through the solution; and *I* shows the *IR* drop through the solution only. The point d is the common breaking point for all the curves. The line to the left of d is heavy because it is common to all three curves.

It is universally accepted that the potential over a pure resistance should drop instantaneously. Curve I, which pictures such a drop, is not vertical as it should be to show an instantaneous drop; this results from a slight lag in the vibrating element of the oscillograph. There can be no doubt, however, that A does not show any drop due to a resistance, which means there could have been no drop due to transfer resistance at the surface of the electrode included in the original potential measured by the direct method. It is clearly evident, on the other hand, that A_I does contain a drop due to resistance. The original potential of A_I contained all of the IR drop shown by I, and from the breaking point, d, the two curves are identical for some distance, and evidently would have remained identical down to the horizontal portion of I had it not been for a slowing-up of the vibrating element as it approached the end of its return swing for curve I. Another way to show that A_I contains the same IR drop as I, and no more or no less, is to measure the vertical distance between A and A_I which is found at all places to be equal to the total drop in I. Such a test was applied to several sets of curves and always held. To show the magnitude of the voltage changes, three constant voltage lines, 1, 2, and 3, were drawn across the film. The distance between 1 and 2 or between 2 and 3 is 40 millivolts. By means of the timing wave, which is for a 120-cycle current, the rate of fall of anode potential may be determined easily.

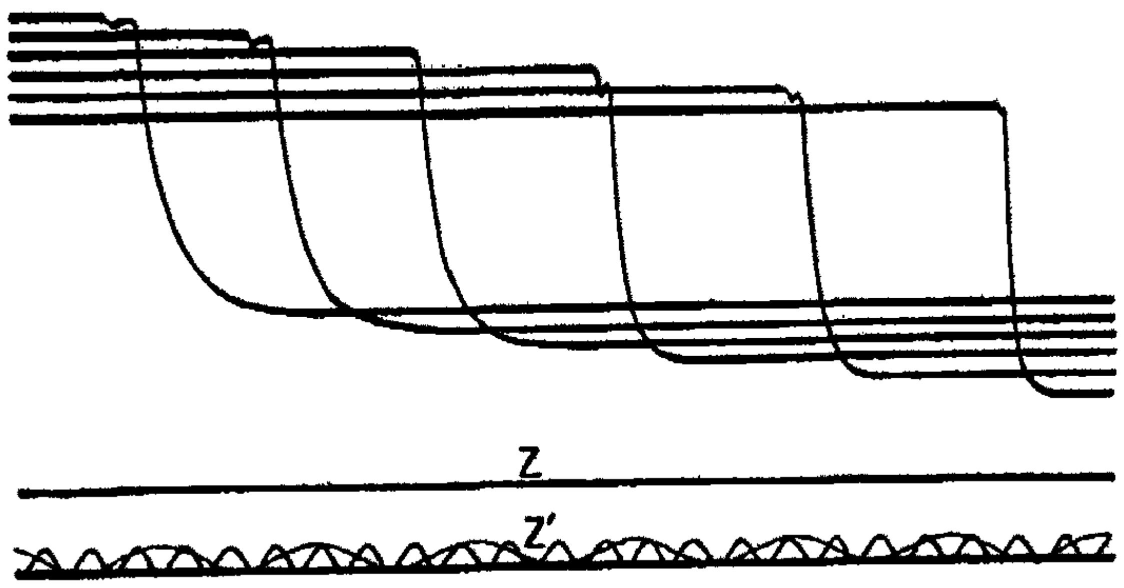

FIG. 3. CURVES TO SHOW THE TIME LAG IN THE VIBRATING ELEMENT OF THE OSCILLOGRAPH

To learn something more definite about the lag of the vibrating element, a series of discharge curves, over a pure resistance, were taken with the same potential applied to the grid but with different balancing potentials so as to bring the curves at different positions on the width of the film. These curves are shown in figure 3. The contact point, P_c, was inserted in different positions so as to cause the break to appear at successive positions longitudinally on the film. The first curve was taken at the highest speed and the last at the lowest; the speeds are represented by the 120-cycle timing waves at the bottom. These curves show that what is really an instantaneous drop is not recorded on the film by a vertical line.

In figure 4 is shown a series of curves obtained with the same film speed, but for different resistances. These all represent potential drops due to pure resistances only, and show similar characteristics. The rate of drop is the same at the start, but slows up distinctly, and in about the same manner, as the element approaches its zero position. From the curves in figures 3 and 4 it would be possible to calculate the lag under a given set of conditions and apply it as a correction. It is evident from these oscillograms that when a curve produced by this oscillograph is analyzed to determine whether it contains a potential due to an *IR* drop, this lag of the vibrating element and variation of the lag with speed of film and displacement of element must be taken into account. The best way to do this is to superimpose the curves to be studied upon a curve representing a pure *IR* drop.

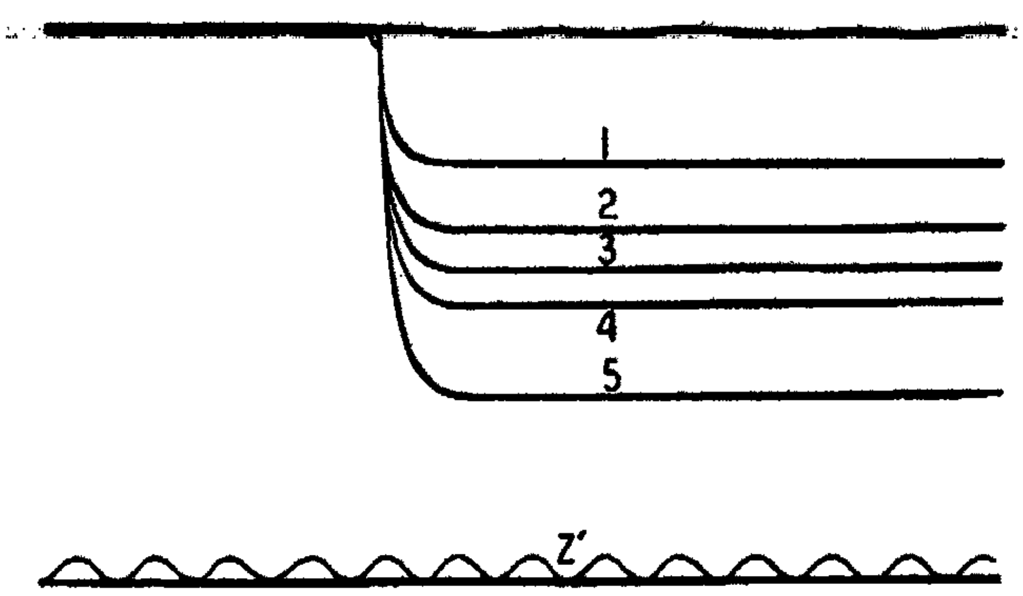

FIG. 4. POTENTIAL DROPS OVER A SERIES OF PURE RESISTANCES

For curve 1, $R = 10$ ohms; for 2, $R = 15$ ohms; for 3, $R = 18$ ohms; for 4, $R = 20$ ohms; and for 5, $R = 30$ ohms.

For very small currents it is not possible to distinguish between curves resulting from electrode depolarization and those caused by *IR* drop. This is evident from the curves in figure 5. These curves were taken for potentials above the decomposition point, but the current density was only 0.00053 amp.

The curves for slightly higher potentials are shown in figure 6. When the depolarization and *IR* drop curves are superimposed, it is just possible to distinguish between them in the case of the highest potential at the top of the film. The drop for I_1 is slightly more rapid at the start than K_1 and soon reaches a constant value, while K_1 continues to drop throughout the whole discharge interval.

A comparison of various types of discharge potentials at both anode and cathode is possible from the curves in figure 7. The current density during the photographing of all the curves in this figure was 0.0094 amp. The *K*

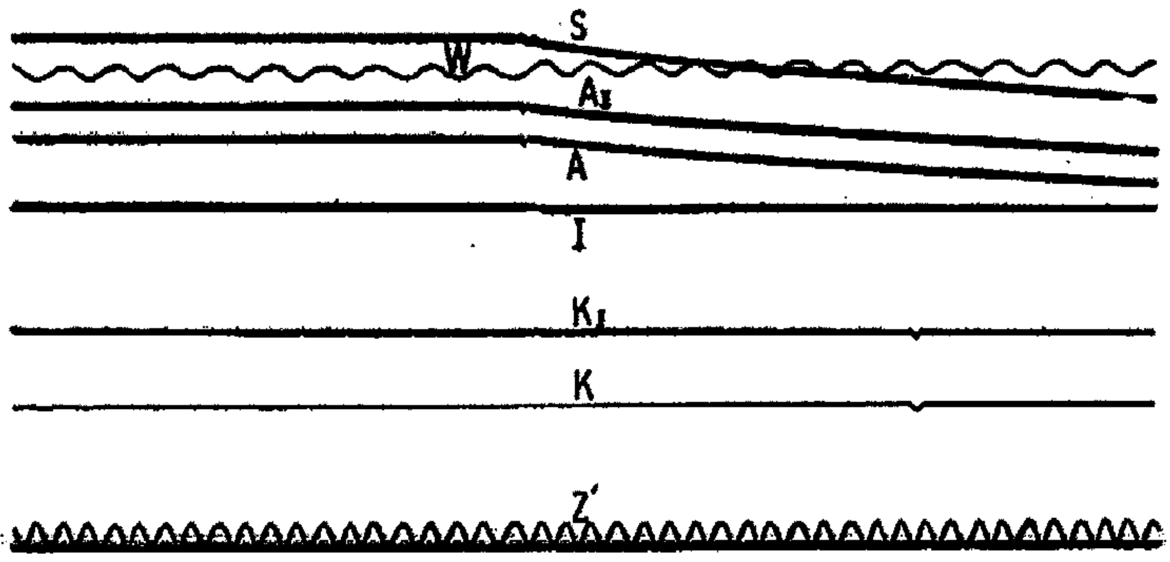

FIG. 5. DISCHARGE CURVES AT CURRENT DENSITY OF 0.00053 AMP.

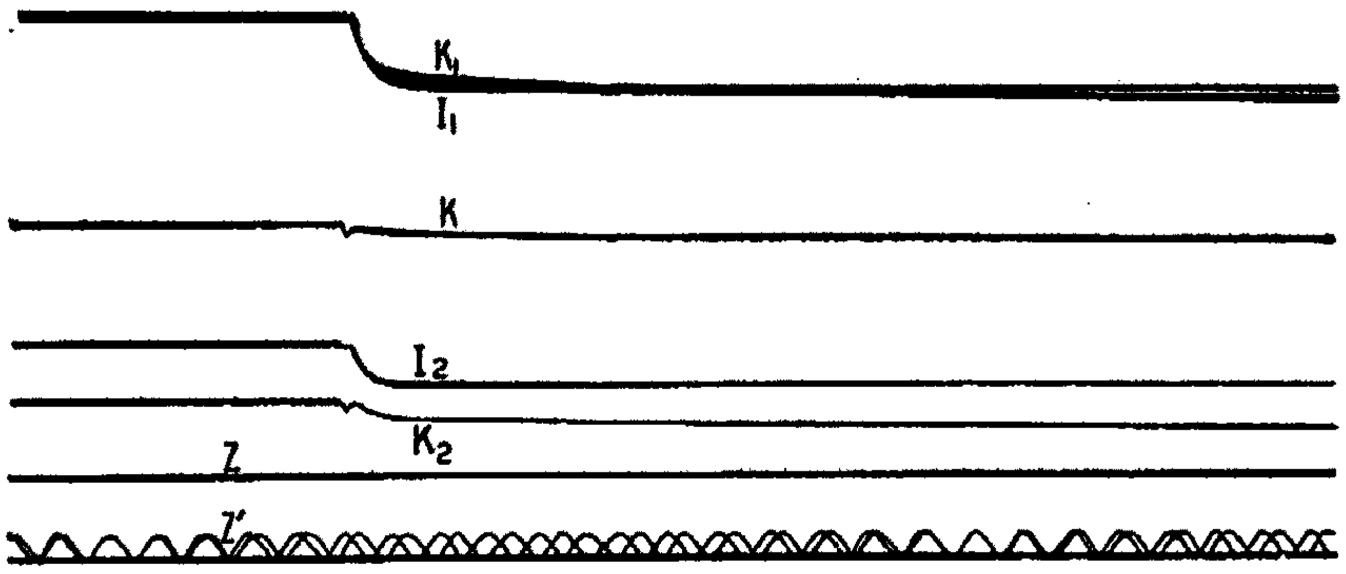

FIG. 6. DISCHARGE CURVES AT CURRENT DENSITIES OF 0.0020 AND 0.0026 AMP.

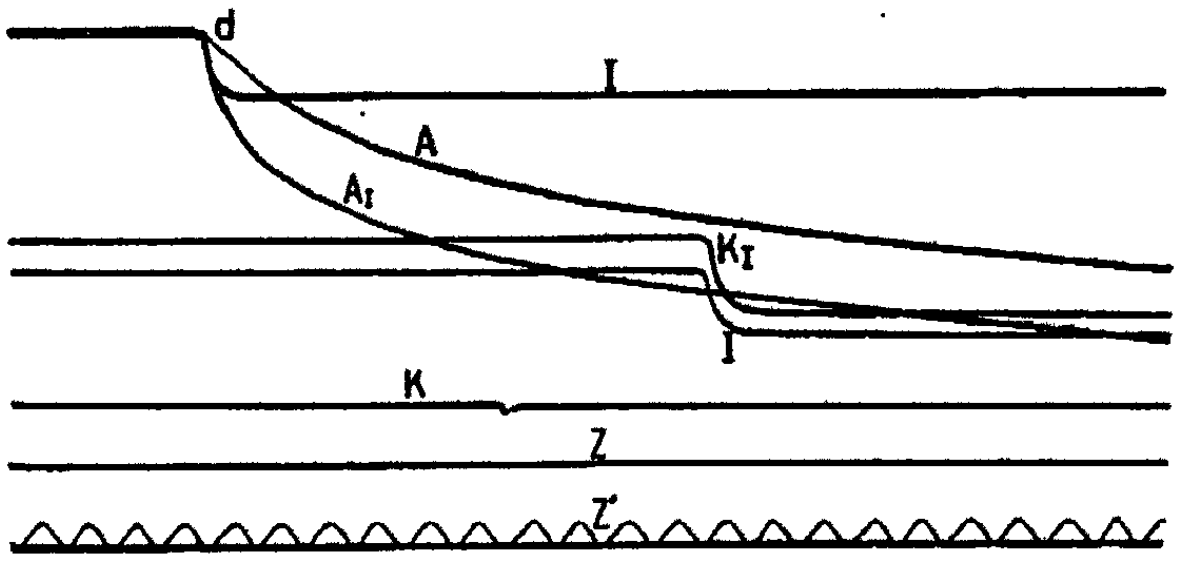

FIG. 7. A COMPLETE SET OF ANODE AND CATHODE DISCHARGE CURVES FOR AN APPLIED POTENTIAL, 2.040 *V*, ONLY SLIGHTLY ABOVE THE DECOMPOSITION POINT

curve shows there was practically no overvoltage at the cathode. The K_t and the I curves are practically identical as they should be, since K shows no overvoltage; but taken separately one would hesitate to say whether K_t represents electrode depolarization or an IR drop. The situation at the anode is clear-cut. There is no doubt that A contains no IR drop. A_t is definitely made up of the sum of the IR drop in I and the electrode depolarization in A. The curves A and A_t are parallel and the distance between them is the IR drop in I.

The curves in figure 8 are for a current density of 0.017 amp., about twice that in figure 7. Here again there can be no question about being able to distinguish between depolarization and an IR drop, especially if the curves are superimposed. There is no indication of an IR drop due to surface resistance of any kind at the anode. The S curve contains the depolarization at both the cathode and anode and also the IR drop through the solution.

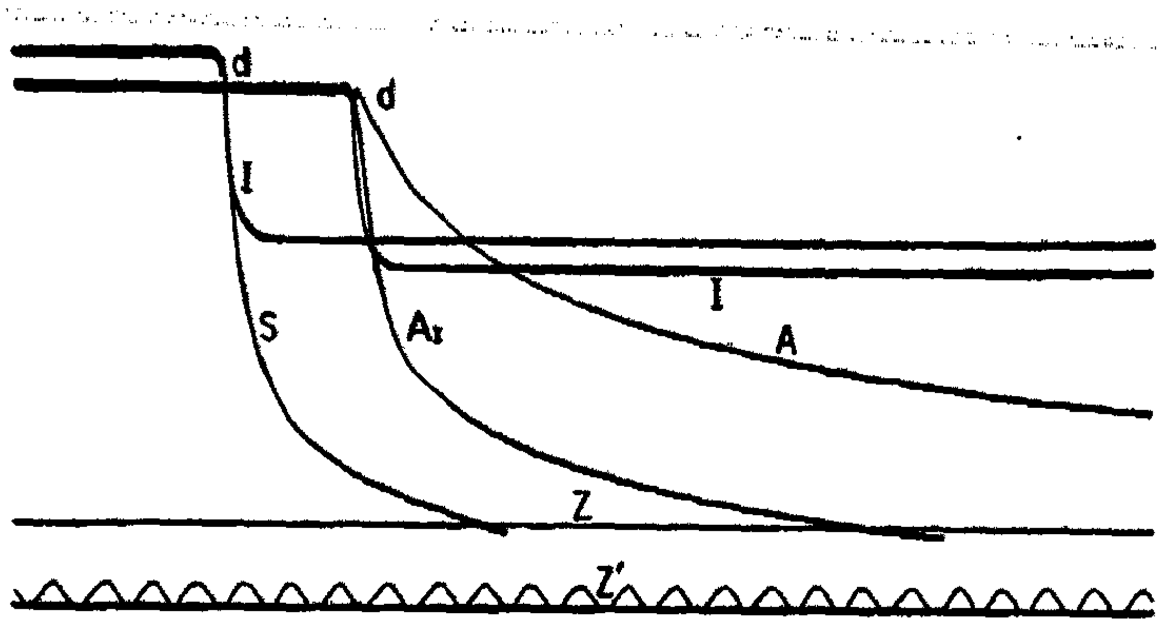

Fig. 8. Discharge Curves for a Current Density of 0.017 amp.

SUMMARY

1. An electromagnetic interrupter is described which makes it possible to open the charging circuit at any desired time interval after charging is started.

2. With this interrupter and accompanying alterations in the oscillograph it is possible to superimpose curves representing various types of potentials as determined by the direct method, and to interrupt the charging circuit at the same point on the film for each.

3. Owing to the lag in the vibrating element, the drop in potential over a pure resistance does not appear vertical.

4. Because of the great lag when the vibrating element has returned nearly to its zero point, it is not possible to distinguish between depolarization and an IR drop when the polarization is less than about 5 millivolts.

5. No curves that represent the potential between an electrode and its own reference electrode, i.e., that contain no known *IR* drop, show any indication of an *IR* drop due to surface resistance.

6. This work substantiates the conclusion arrived at in several earlier papers from this laboratory, that there is no transfer or surface resistance at platinized platinum electrodes in 2 *N* sulfuric acid.

The junior author wishes to acknowledge his indebtedness to the China Foundation for the Promotion of Education and Culture, for the granting to him of a fellowship which made it possible for him to continue his research work at the University of Michigan.

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NEW BOOKS

Die Alkalichloridelektrolyse in Diaphragmazellen. By G. Angel. 19 x 13 cm.; 126 pp. Berlin: Verlag Chemie, G. m. b. H., 1933. Price: 12 M.

In this monograph the author has reëxamined the whole basis of the theory of the electrolysis of alkali chloride solutions in diaphragm cells. It is shown that when a true steady state has been established the current efficiency can be expressed as a function of the alkali concentration in the catholyte; the exactness of the relations deduced has been tested by numerous experiments with sodium chloride solutions in cells of the horizontal diaphragm type. Physical properties of the electrolyte have been measured under various conditions, and the density, viscosity, and conductivity of both anolyte and catholyte at various temperatures are related to the alkali concentration of the catholyte. Comparison of the theoretical relations for potassium and sodium chlorides indicates that, starting with solutions saturated at room temperature, the current efficiency in the steady state should be lower in the former than in the latter case. This conclusion, which is at variance with previously accepted statements, is shown to be borne out by experimental results.

The theoretical discussions and experimental results constitute an important contribution to the study of this complex subject and should prove of considerable value in the further development of technical cells and in the control of their operation. The main conclusions are summarized clearly at the end of each section of the book, and the experimental data are set out in numerous tables and graphs.

H. J. T. Ellingham.

Die moderne Atomtheorie. Die bei der Entgegennahme des Nobelpreises 1933 in Stockholm gehaltenen Vorträge von W. Heisenberg, E. Schrödinger, and P. A. M. Dirac. 22 x 15 cm.; 45 pp. Leipzig: Verlag S. Hirzel, 1934. Price: 2.50 RM.

This collection of three Nobel lectures on related subjects deals, in succession, with the uncertainty principle, with the fundamental conceptions of wave mechanics, and with the theory of electrons and positrons. The subjects are dealt with in a broad and general way, yet in sufficient detail in each case to bring out the essential features. The advantage which every reader obtains from such a book depends on the mental background which he brings to it, but all physical chemists who are acquainted with the general notions of generalized coördinates, the quantum theory, and experimental physics will find these profound yet clearly written expositions of considerable interest, and will gain from them a picture of the broad features of certain aspects of modern atomic theory.

J. R. Partington.

Pflanzenthermodynamik. By Kurt Stern. 22 x 15.5 cm.; xi + 412 pp. Berlin: Julius Springer, 1933. Price: unbound, 32 RM; bound, 33.20 RM.

This book is divided into two parts. The first is an exposition of the principles of thermodynamics; the second a description of their application to processes occurring in plants. In the former the author's stated object is to concentrate on those parts of the subject with a direct application to plants to the exclusion of those with little or no bearing on botany, but it is difficult to see in what respect this object has been achieved. The method of treatment, in fact, appears to be essentially a condensed version of that of Schottky, Ulich, and Wagner, but brevity has been gained only at the expense of lucidity and accuracy. The best feature of the treatment is the discussion of the most general physical principles, such as the first and second laws of thermodynamics, chemical equilibrium, and osmotic equilibrium. There is also a good, if out of place, review of photochemistry, which is not thermodynamics at all. The treatment of other topics is less fortunate. For instance, whereas emphasis is rightly laid on the distinction between total work and useful work (Nutzarbeit), the difference is not clearly defined. Again the well-known formula obtained for the efficiency of a Carnot cycle is applied to cycles of other types, for which its validity has not been demonstrated. This error occurs in almost all elementary textbooks, but the present book is not at all elementary. In fact the reviewer found it heavier reading than almost any of the most advanced treatises on thermodynamics.

The applications described in the second part of the book are of great interest. It is explained that, owing to the great experimental difficulty of obtaining accurate thermodynamic data with plant materials, only a low order of accuracy is possible. This being the case, surely a briefer and easier treatment would have been adequate as well as more attractive.

To sum up, the book should interest the reader whose chief concern is thermodynamics, by showing the importance of the subject for botany. It is, on the other hand, less likely to attract the botanist to a study of thermodynamics than to frighten him away from it.

E. A. Guggenheim.

The Science of Radiology. Edited by Otto Glaser. 450 pp. Baltimore: Charles C. Thomas, 1933. Price: $4.50.

This collection of twenty-five papers on the various phases of the science of radiology is published under the auspices of the American Congress of Radiology and the editorship of Dr. Otto Glaser, who also contributes the first two papers on the history of the discovery of Roentgen rays and on the discovery of radium. The succeeding ten chapters are devoted to x-rays, including one by D. L. Webster on Roentgen-ray physics, one by W. D. Coolidge and E. E. Charlton on Roentgen-ray tubes, and one on therapy by U. V. Portmann. Several chapters deal with radium therapy and technique. Miscellaneous chapters treat Roentgen-ray protection, teaching of radiology, and industrial radiology. Leaving therapy entirely, the last two chapters comprise one by A. H. Compton on cosmic rays and one by William Seifriz on the mitogenic rays which he calls "Gurwitsch" rays. The author is not convincing in his defense of the reality of this much questioned type of radiation. Quantized energy relations are wholly neglected, though evidently important in attempting to decide whether light of ultra-violet wave length may be invoked as a cause of the observed phenomena.

The entire collection is highly creditable to the contributors and to the editor and will be indispensable to all who are interested in radiotherapy.

S. C. Lind.

Electrokinetic Phenomena and their Application to Biology and Medicine. By Harold A. Abramson. American Chemical Society Monograph. 15.5 x 23.5 cm.; 331 pp.; 106 figs. New York: The Chemical Catalog Company, Inc., 1934. Price: $7.50.

This book will fill a great need in the field of physical chemistry and of its allies, biochemistry and biophysics. The reviewer has, for a number of years, been working in the field of electrokinetics and has acutely felt the need for a monographic treatment of the literature, which, until this volume appeared, has been scattered through a great variety of texts and journals, many of which are almost inaccessible to the average worker.

Electrokinetics deals with the electrical behavior of the phase boundary at interfaces. The solid-liquid and liquid-liquid interfaces have been most widely studied, although unquestionably solid-gas and liquid-gas interfaces show similar phenomena. At these interfaces, electrokinetics is concerned with the so-called Helmholtz double layer, and should not be confused with the Nernst, or thermodynamic, or membrane potential.

The book opens with an excellent "Historical" chapter which adequately covers the literature from Reuss (1808) to Helmholtz (1879). This is followed by "Early theory and related experiments," where the contributions of Helmholtz, Quincke, Wiedemann, Lamb, von Smoluchowski, Perrin, Pellat and others, in building up the theory of a rigid double layer are considered. These chapters are followed by others on "Early confirmation of theory" and an excellent discussion of "Methods." A discussion of "Recent theory and related experiments," in which the reviewer was delighted to find a thorough treatment of the diffuse layer theory of Gouy and Debye and Hückel, closes the theoretical section.

Later chapters deal with "Proteins and some related compounds," "General effect of salts on inert surfaces," "Inorganic surfaces," "Organic surfaces," "Gases," "Blood cells, spermatozoa, tissues, etc.," and "Bacteria, antibodies, viruses, and related systems." An appendix follows, which includes a key to the mathematical symbols used in the formulas, a table of the numerical value of the various constants and factors, and a list of patents covering various phases of electrokinetic behavior. Author and subject indices close the volume.

Throughout the book the mathematical treatment is excellent. The author, while himself actively doing research in this field, presents impartially his own viewpoint and the viewpoints of others. One sometimes even wishes he were not such an impartial critic.

As one glances through the literature references one is impressed with the fact that the vast majority date since 1920. Industry, biology, and medicine have all profited by the use of electrokinetic technics. They will profit still more as workers in this field are multiplied, and this book will be a great assistance to that end. It is highly recommended to all who are interested in the solution of the problems of interfaces. It should be in all chemical, physical, and biophysical libraries. The price will be the only deterrent to its purchase by many individuals.

Ross Aiken Gortner.

Physico-chemical Practical Exercises. By W. N. Rae and Joseph Reilly. 19 x 13 cm.; xiv + 276 pp. London: Methuen and Co., 1934. Price: 7s. 6d.

The authors of the well-known book, "Physico-chemical Methods," now in its second edition, which is so useful to the advanced worker for reference, have here given us a much smaller volume, intended for students working for an honors degree in chemistry.

The book begins with a mathematical consideration of error, nomography, and calibration of apparatus. Important as this is, it would have been better, in the reviewer's opinion, to have placed this section at the end of the book. The student beginning work on physical chemistry is too apt to concentrate on the elimination of small errors and unknowingly introduce larger ones.

The experiments described, seventy-three in all, are many of them usual in such textbooks; there are, however, interesting additions, e.g., in surface tension, Jaeger's method, viscosity by the falling sphere, Rast and Menzies' methods in determination of molecular weight, and the use of the glass electrode and valve electrometer. On the other hand, exercises not usually found in an elementary textbook are described: e.g., measurement of gas viscosity, vapor pressures, heat conductivity of gases, and the Nernst calorimeter.

Theory is introduced where necessary. There are seventy-four diagrams in the text, some of which might be improved, e.g., the Pulfrich refractometer, capillary electrometer etc.

The student who has the time in his degree course to work through all these experiments will have laid an excellent foundation for a study of physical chemistry and the book, at its reasonable price, can be strongly recommended.

W. H. Patterson.

Kristallchemie. By O. Hassel. (Band 23 of Wissenschaftliche Forschungsberichte, Naturwissenschaftliche Reihe. 22 x 15 cm.; vii + 114 pp. Dresden and Leipzic: Steinkopff, 1934. Price: unbound, 9 RM; bound, 10 RM.

Until a year or so ago many of the existing treatises on x-rays and their applications to crystal physics and chemistry were rather out of date, and some of the latest views were only to be found in isolated papers. New editions of well-known works have now appeared, and in addition we have before us a small book by Dr. Hassel dealing with what is generally referred to in English as chemical crystallography. Dr. Hassel's own researches on coördination compounds are his passport to this field, and in *Kristallchemie* he has given a lucid account of the laws that may be deduced from crystal structure determinations by means of x-rays.

W. L. Bragg was the first to deduce approximate atomic radii from crystal-structure determinations and this has been followed in later years by the elaborations of Goldschmidt, Pauling, and Zachariasen. Using the figures for atomic size, and electrostatic energy considerations, Pauling has also deduced a set of rules of great importance in structure determination. Dr. Hassel's book deals with all these points, and with many more, of which the crystal chemistry of the silicates and of the intermetallic compounds may be mentioned.

The treatment throughout is simple and avoids all reference to the various technical methods of obtaining results. In this respect it is particularly valuable to physical chemists, particularly at a time when questions of atomic binding are receiving so much attention. It is a book to be read side by side with Sidgwick's *Covalent Link*. There are few illustrations, which is perhaps a pity, but this consideration was no doubt dictated by the fact that the book is one of a series.

J. T. Randall.

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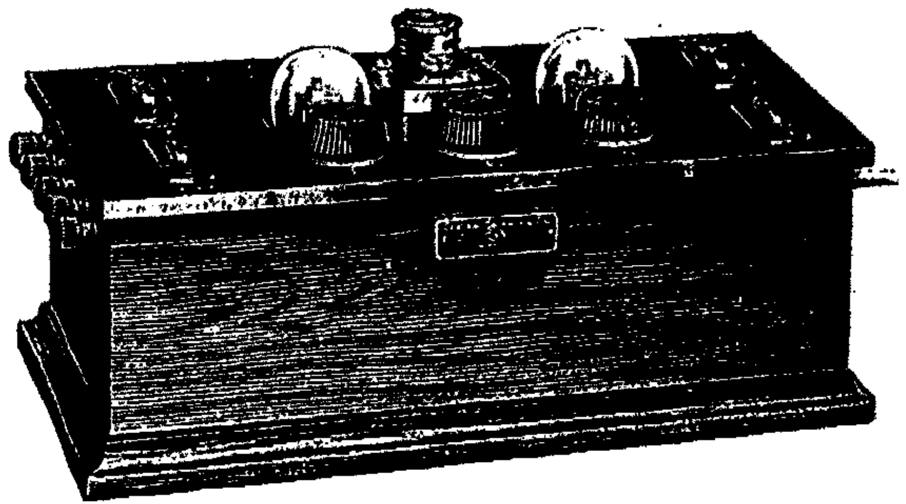

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A STUDY OF THE ACTION OF ACIDS ON ZINC AT PRESSURES OF FROM ONE TO THIRTY THOUSAND ATMOSPHERES

THOS. C. POULTER AND GLEN E. FRAZER

Department of Physics, Iowa Wesleyan College, Mount Pleasant, Iowa

Received June 27, 1932

INTRODUCTION

While much of the data in this article is of a qualitative nature, the authors thought that the material was of sufficient interest to be published.

The importance of pressure as affecting chemical equilibrium has long been recognized, and many equilibrium conditions can be calculated to a high degree of accuracy. In many cases it is experimentally impossible to obtain the calculated conditions necessary for equilibrium. Such a case is that of the reaction of acids on zinc. The electrical potential exhibited by the zinc electrode as compared with that of hydrogen is a measure of the tendency of the reaction $H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$ to proceed in the direction indicated.

In order to calculate the pressure necessary to bring this reaction to equilibrium:

$$E = \frac{RT}{NF} \ln K = \frac{0.05915}{N} \log K \qquad E = 0.7581$$

$$1/2\, Zn + H^+ = 1/2\, H_2 + 1/2\, Zn^{++}$$

$$0.7581 = 0.05915 \log K = 0.05915 \log \frac{a_{Zn}^{\frac{1}{2}}\, P_{H_2}^{\frac{1}{2}}}{a_H}$$

from which we find that

$$K = 6.45 \times 10^{12}$$

If we have a solution containing zinc and hydrogen ions at unit activity and immerse in it a strip of pure zinc, it may be calculated from this value of the equilibrium constant that a pressure of 2.53×10^{25} atmospheres would be required to establish equilibrium.

The activity of the hydrogen ion has been studied as a function of hydrogen pressure by Hainsworth, Rowley, and MacInnes (3), and found to decrease by only 0.4 per cent at 500 atmospheres and 8.8 per cent at 1000 atmospheres.

The purpose of this investigation was to study the abnormal decrease in the rate of reaction of acids on zinc reported by V. N. Ipatiev and his coworkers (4, 5) and also studied by F. E. Brown (2). Ipatiev and his coworkers reported that the velocity of this reaction is reduced to a small per cent of its normal value at pressures as low as 50 atmospheres and that equilibrium conditions are reached at less than 1000 atmospheres. A reversal of the reaction in some cases is reported.

APPARATUS AND PROCEDURE

A series of experiments was run by the authors in which the pressure measured was built up by the hydrogen evolved during the reaction. For these experiments sticks of pure zinc, F, were placed in a very thin bottom glass container A (figure 1), the remaining space being filled with water. The top was then sealed with wax to prevent the acid from coming in contact with the zinc until it was desired to start the reaction. The glass container thus filled with zinc and water was supported on a shoulder in in the upper portion of the pressure bomb. The pressure bomb was lined with an acid-proof wax and filled with 6 N sulfuric acid. Two copper tubes were sealed through the cap, one of which led to a pressure gauge and the other to a hydraulic pump. The pressure could be released by means of a valve at E.

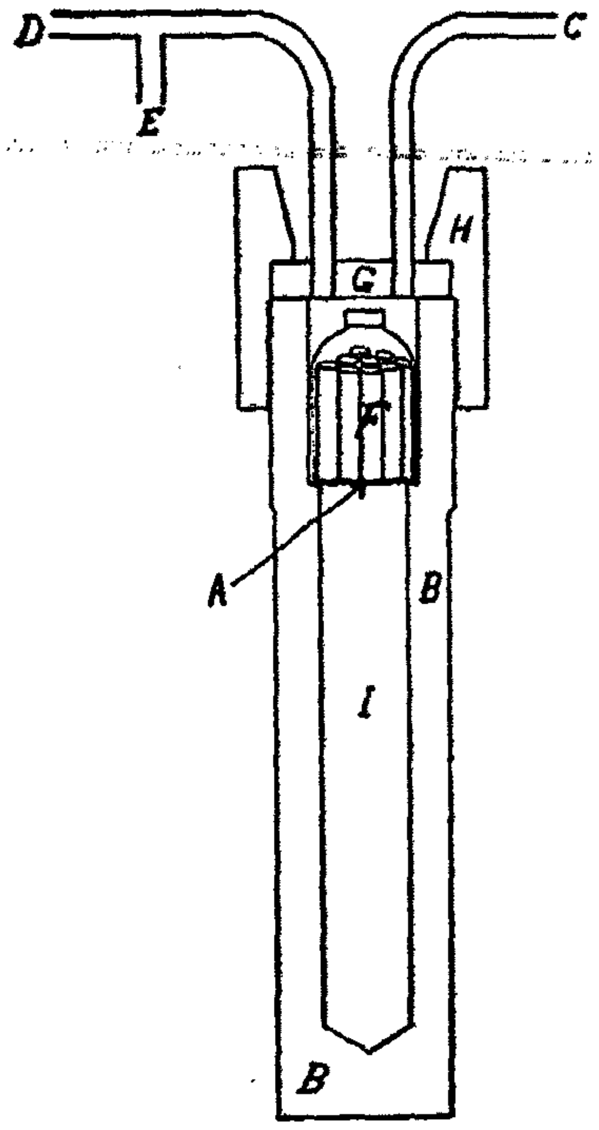

FIG. 1. PRESSURE REACTION BOMB

All of the copper tubing and the pressure gauge was filled with oil, leaving very little free space in the pressure system. After all materials had been placed in the bomb and the cap screwed in place, the zinc was brought into contact with the acid by jarring the bomb against a steel block, thus causing the zinc sticks to break through the thin bottom of the glass container. The pressure was read at intervals of half a minute. This assembly of apparatus permitted the reacting materials to be shaken at frequent intervals. The surface of the zinc sticks was scraped and rinsed with ether to remove all traces of dirt and grease.

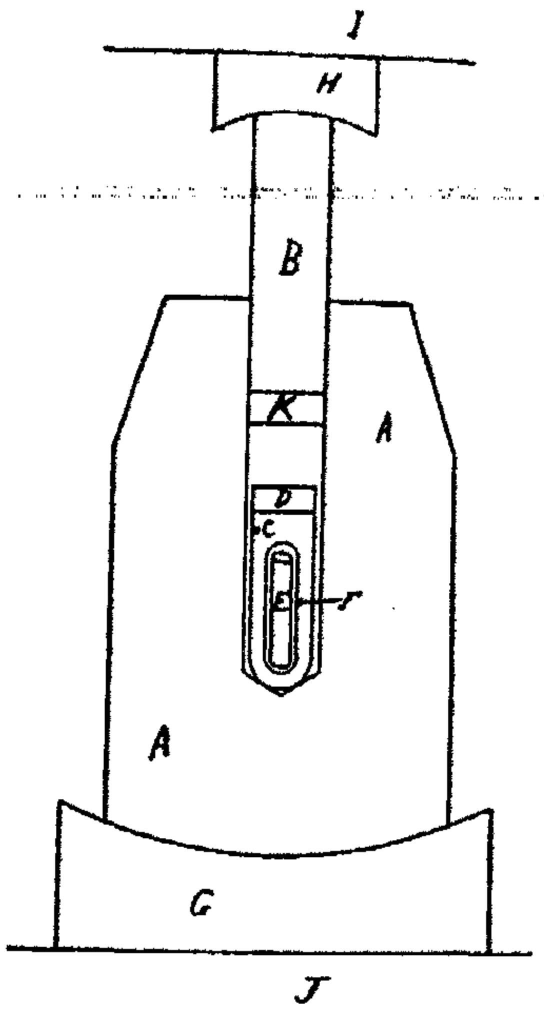

Fig. 2. Pressure Cylinder

The pressure gauge employed in these experiments had a range of only 350 atmospheres. For the purpose of making the measurements at higher pressures a much heavier pressure bomb (figure 2), was constructed, which had an inside diameter of 15 mm. and a capacity of 17 cc. Leaking was prevented by placing a close fitting rubber stopper, K, in the cylinder ahead of the piston B. The curvature of the top of the piston and the bottom of the cylinder are sections of spheres having a common center for convenience in lining the cylinder up in the press. The blocks H and G rest directly in contact with the platens of the hydraulic press. The pressure on the reaction was determined as described in another article by one of the authors (6). For these experiments the zinc, E, was sealed in a glass capsule, F, in order to prevent it from coming in contact with the acid until the assembly was completed. The acid, together with the capsule containing the zinc, was placed in a short rubber cup, C, which was stoppered and placed in the pressure cylinder.

The remaining free space was filled with a light paraffin oil. The glass capsules containing the zinc were broken at from 8000 to 12,000 atmospheres pressure. The zinc sticks which had been previously weighed were allowed to remain in contact with the acid for 30 minutes at 20°C. They were then removed as rapidly as possible, washed free from acid, dried, and again weighed. The loss in weight could be thus determined for various pressures.

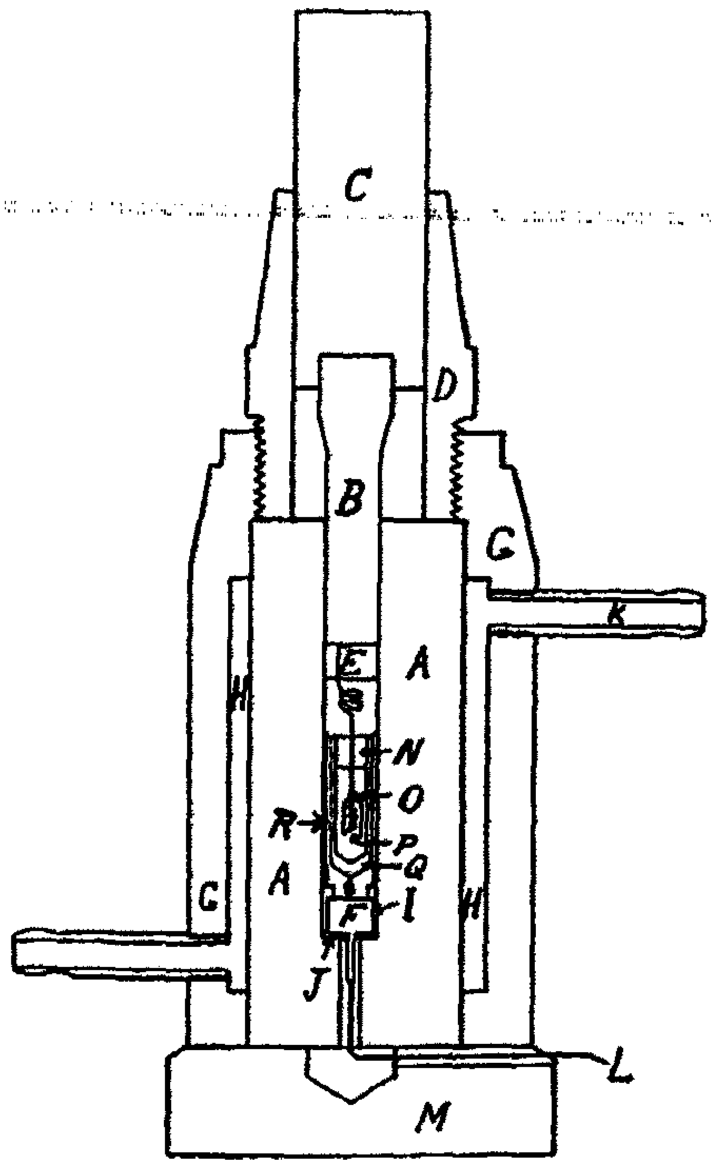

Fig. 3. Pressure Cylinder

Attempts were made to measure the E. M. F. of a cell composed of the zinc and hydrogen electrodes in normal sulfuric acid. In order to do this it was necessary to construct a pressure cylinder in such a way that an electrode could be insulated through the wall of the cylinder and yet withstand the high pressures without leaking. For this purpose the pressure cylinder and cell assembly shown in figure 3 were constructed. The zinc electrode, Q, was made in the form of a cup into which the sulfuric acid was placed.

The platinized platinum electrode, P, was surrounded by a glass apron, O to prevent contact with the zinc electrode. It was held in place by a rubber stopper, N, inserted in the top of the zinc cup. A mica tube, R, prevented the zinc from coming in contact with the cylinder wall. The free space in the pressure cylinder was filled with a light paraffin oil and the pressure developed and measured as with the previous cylinder. This cylinder was equipped with a water jacket for temperature control. Water from a thermostat was circulated through the water jacket and the platens of the hydraulic press.

EXPERIMENTAL RESULTS

In the experiments where the evolved hydrogen was allowed to build up the pressure, about twenty minutes was required for pressures of 350 atmospheres to be developed. A few typical pressure–time curves are shown in figure 4. In experiment No. 16 the initial conditions were made as nearly identical with those of No. 15 as possible. However, instead of allowing the reaction to take place under its own gradually increasing pressure, the pressure of the system was regulated as follows by means of an oil pump. The reaction was started at 34 atmospheres and the hydrogen allowed to build the pressure up to 68 atmospheres, at which time the pressure was raised by means of the pump to 163 atmospheres. The evolved hydrogen was then allowed to build the pressure up to 202 atmospheres. The pressure was then released to 34 atmospheres and allowed to build up to 116 atmospheres. The experiment was then discontinued after having extended over the same length of time as No. 15.

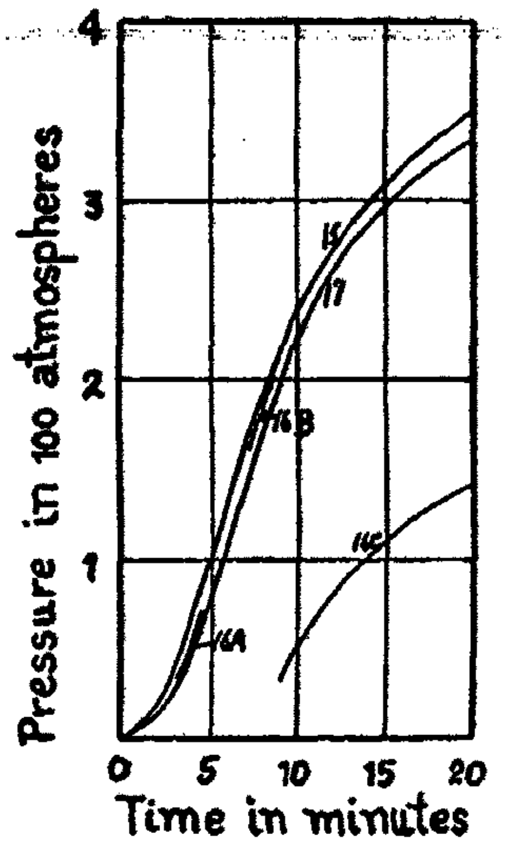

FIG. 4. TIME-PRESSURE CURVES

The reaction in the next pressure cylinder employed was followed by means of the loss in weight of the piece of zinc during the time it was in contact with the acid. The pieces of zinc were all 5 mm. in diameter and 25 mm. in length so as to expose the same surface to the acid. In all cases where the pressure was not higher than 8000 atmospheres the loss in weight of the zinc was from 0.5 to 1.0 g. These experiments were run at pressures of from 300 to 8000 atmospheres, and the loss in weight was found to be independent of the pressure. However, if the pressure was maintained at above 9000 atmospheres, the loss in weight of the zinc was never more than 0.02 g.

The assembly shown in figure 3 was then constructed and E.M.F. determinations were attempted, but with little success, particularly at the higher pressures as the results fluctuated over a large range. However, the qualitative results proved to be very interesting. Since E.M.F. measurements were so unreliable, a galvanometer was substituted for the potentiometer. The pressure was then varied between 1 and 30,000 atmospheres. Between 8000 and 9000 atmospheres a marked increase in current was noticed, particularly if the pressure was raised rapidly. The current again returned to its normal value if the pressure was held constant at its new value. Above 9000 atmospheres the value of the current dropped almost to zero in those cases in which only a short time elapsed between the assembling of the cell and the attainment of this pressure. The value of the current remained at this low value as long as the pressure was maintained above 8900 atmospheres.

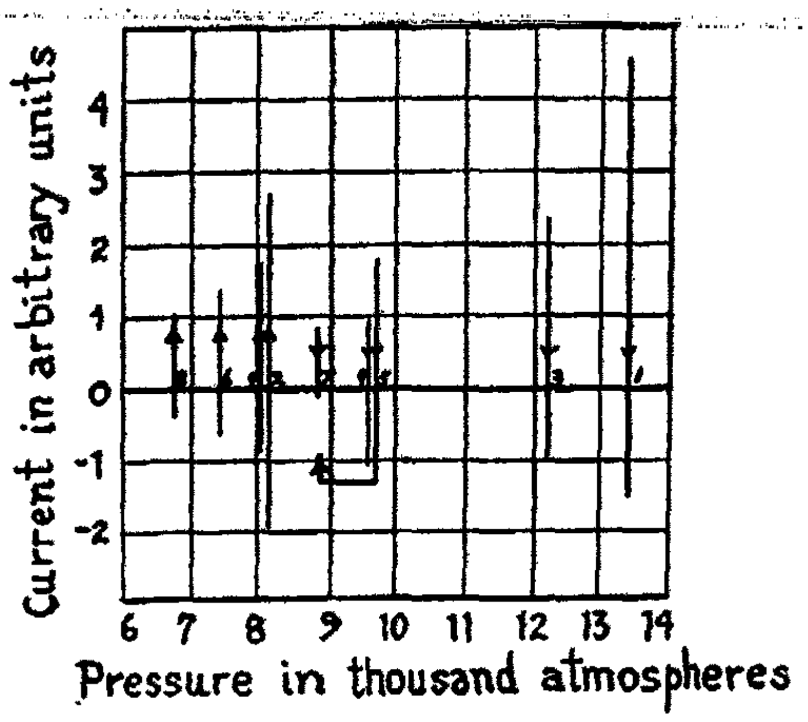

FIG. 5. REVERSAL OF CURRENT AT CONSTANT PRESSURE FOLLOWING A PRESSURE CHANGE

In cases where several minutes passed before a pressure of 9000 atmospheres was reached, the current dropped to zero and reversed direction, and a small current was built up in the opposite direction. In such cases the original direction of the current was obtained by dropping the pressure to below 8400 atmospheres and was again reversed by raising it to above 8900 atmospheres. In one case the direction of the current was reversed nine times. Figure 5 shows the change in current following a change in pressure. The segments in this figure are numbered in the order in which they were obtained experimentally, and each segment represents the change in current at constant pressure but immediately following a pressure change. For instance, the pressure was built up to over 13,000 atmospheres, at which time the current changed as indicated by segment one; then the pressure was released to a little over 8000 and the current changed as indicated by segment two and so on. The pressure changes in each case were made rapidly from the pressure represented by the position of the previous segment of the curve. These measurements were made at 20°C.

The pressure at which reversal takes place depends upon the temperature. The reversal of current takes place at 7000 atmospheres if the temperature is 5°C.

In all cases following a reversal of current the odor of hydrogen sulfide was distinctly noticed upon opening the cylinder, but in cases where no reversal had occurred hydrogen sulfide was not detected.

No reversal was obtained if bright platinum was used instead of platinized platinum for the hydrogen electrode. Moreover, no reversal was obtained with either type of electrode if hydrochloric acid was used instead of sulfuric acid.

DISCUSSION OF RESULTS

At low pressure the evolution of hydrogen from the surface of a metal during the action of an acid upon it keeps the surface freed from material that would tend to prevent the acid from coming into contact with the metal surface and at the same time keeps the acid stirred.

If this same reaction is carried out under pressure, the hydrogen is almost, if not completely, dissolved in the acid as fast as it is formed and there are at most only a very few small bubbles produced. Therefore, little or no circulation occurs. It was found that a very slight trace of grease on the surface of the zinc, such as would be produced by handling with apparently clean hands, would cause a very marked retarding of the speed of reaction when the system was under pressure. The normal reactivity could be restored by washing the zinc in ether. Another effect directly due to lack of stirring is that of local decrease in acid concentration and in increase in salt concentration at the surface of the metal. The decided decrease in the slopes of the curves of figure 4 as the reaction proceeds are due largely to the change in concentration of the acid rather than to any effect due directly to pressure. This is apparent from the curves for experiment No. 16 as shown in figure 4. If the velocity of the reaction were affected by pressure, the three segments of curve 16 should be parallel to those portions of number 15 corresponding to the same pressure, but since they are parallel to those portions corresponding to the same time position, it is apparent that pressures up to 350 atmospheres have little effect upon the reaction of sulfuric acid on zinc.

Ipatiev and his coworkers report that in some cases 122 days were required for the zinc–sulfuric acid system to build up a pressure of 350 atmospheres. That pressure was obtained by the authors with the same reactants within twenty minutes. The difference is likely, owing to the fact that the authors were able to fill all of the space in the container with liquid and that the surface of the zinc in the experiments herein described was free from all traces of grease, whereas Ipatiev took no such precautions. The authors were also able to shake the reacting materials at frequent intervals.

It was desired to investigate the effect of higher pressure upon the action of sulfuric acid in zinc, since no marked effects directly due to pressure had been observed up to 350 atmospheres.

The method of allowing the reaction products to build up the pressure does not lend itself to very accurate measurements, particularly when the pressure changes are large, because of the considerable time involved, the accompanying changes in concentration, and the change in volume of the system when the metal goes into solution in the form of its salt (5). Other factors are the penetration of hydrogen through the steel (1) and the compressibility of the heterogeneous system at high pressure. An attempt to correct for all of these factors would not lead to dependable results.

A more dependable method is that of measuring the decrease in weight of a piece of zinc of definite size and shape under controlled conditions.

While the activity of the hydrogen ion is reduced by 8.8 per cent at 1000 atmospheres of hydrogen pressure it might be supposed that the above reaction would be correspondingly slowed down; however, this decrease in activity is not a direct result of pressure, but is due to the solubility of hydrogen at that pressure, a condition which cannot be accomplished until after the reaction has proceeded for considerable time.

It is of interest that it is impossible under these conditions to acquire a higher concentration of dissolved hydrogen than that acquired at about 9000 atmospheres, because at that pressure hydrogen readily passes through the walls of a steel container.

The loss in weight of 0.02 g. or less for cases where the pressure was maintained above 9000 atmospheres can be accounted for by the time required to remove the zinc from the acid after releasing the pressure. The reason for the sudden decrease in the reaction at 9000 atmospheres is fairly clear; at this pressure little or no loss in weight of zinc would be expected, since at pressures above 9000 atmospheres at 20°C. the solution solidifies, owing to the formation of ice VI, thus preventing the migration of the acid to the surface of the zinc.

The irregularity of the potential of the zinc–hydrogen cell is probably due to the irregularity of local concentration conditions around the electrode and the reduction of sulfuric acid to hydrogen sulfide at the platinized platinum electrode. This is indicated by the strong odor of hydrogen sulfide when the cells are opened. It also accounts for the reversal of the current at pressures above that necessary for the formation of ice VI. The fact that no reversal occurs when a bright platinum electrode is used or when hydrochloric acid is used instead of sulfuric acid also indicates that the reaction $4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$ takes place at the surface of the platinized platinum electrode. The reaction is catalyzed by the platinized platinum and the high pressure. Because of the smaller volume of the products of this reaction it would be favored by pressure. The formation of hydrogen sulfide probably would not account for the reversal of polarity if it were not for the fact that the formation of hydrogen is practically stopped by the solidification of the acid solution.

As the pressure is quickly raised past that necessary for the formation of ice VI an increase in temperature occurs, owing to the change in volume. This would account for the sudden increase in current occurring at that pressure. Upon standing for a few minutes this heat energy is conducted through the cylinder walls and the solution solidifies owing to the formation of ice VI, whereupon the current drops to its low value. Further evidence that the acid solution is solidifying is the fact that the current is reversed by a pressure of 7000 atmospheres if a temperature of 5°C. is employed. A relatively large change in volume takes place within the same pressure range as the reversal of current, for further proof of the formation of a solid modification. These two pressures approximate those found by Bridgman for the formation of ice VI at the corresponding temperature.

SUMMARY

The velocity of the reaction $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ is affected very little by pressure up to 8900 atmospheres. Between that pressure and 30,000 atmospheres very little reaction occurs, probably owing to the inability of the acid to migrate to the surface of the zinc and to local concentration effects. An electric cell having zinc and hydrogen electrodes has its polarity reversed by a pressure sufficient to form ice VI. At a pressure of 8900 atmospheres at 20°C. in the presence of platinized platinum the reaction $4H_2 + H_2SO_4 \rightarrow H_2S + H_2O$ is predominant so long as a hydrogen concentration remains.

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THE SYSTEM PYRIDINE-ACETIC ACID. III

ELECTRICAL CONDUCTANCE

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Received August 23, 1934

In an earlier paper by one of the authors (5), the effect of temperature on the viscosity of mixtures of pyridine and acetic acid was reported. In this work it was found that this system showed a sharp maximum viscosity in the neighborhood of 80 mole per cent acetic acid, the maximum persisting at this same composition for temperatures as high as 80°C.

In a more recent paper by the present authors (6), the melting point–composition relations of this system were reported. The melting point–composition diagram shows evidence of the existence of two eutectic mixtures and two complexes. One complex, showing 50 mole per cent acetic acid, had a melting point of −48°C. The second complex had a composition between 80 and 85 mole per cent acetic acid, with an incongruent melting point above −43°C. The first of these complexes is in no way shown by the viscosity–composition curves for this system. The second complex occurs at a composition in the neighborhood of the mixture having maximum viscosity.

In view of this lack of agreement between the melting point and viscosity data for this system, we have measured the electrical conductance over the entire range of composition for this system, to determine if this property is related to either of the properties previously reported.

The value of conductance measurements as a criterion for complex formation has been discussed by Kendall and Booge (1). They state that a maximum conductance always occurs in the vicinity of that composition corresponding to an unstable complex compound. Sakhanov (3) has also used conductance data as a means of identifying complexes existing in various systems.

Conductance measurements have been made on this system by Trifonov and Cherbov (7) and by Sakhanov (4). Neither Trifonov and Cherbov's nor Sakhanov's data extend completely over the entire range of composition.

APPARATUS

Conductance measurements were made with the usual Wheatstone bridge assembly, supplied with alternating current at 1000 cycles per second. The ear phones were tuned to the same frequency. The accuracy of the slide wire and resistances was checked by balancing resistances against each other. A cylindrical conductivity cell with freshly platinized platinum electrodes was used for all measurements.

TABLE 1

The specific conductance of pyridine and acetic acid mixtures

ACETIC ACID	SPECIFIC CONDUCTANCE × 10³				
	At 0°C.	At 9.9°C.	At 19.9°C.	At 29.9°C.	At 40.1°C.
mole per cent					
0.000	0.0012	0.0013	0.0014	0.0015	0.0021
12.247	0.0035	0.0042	0.0049	0.0053	0.0061
25.033	0.0134	0.0163	0.0200	0.0231	0.0266
37.414	0.0408	0.0524	0.0652	0.0791	0.0933
49.678	0.1781	0.2295	0.2863	0.3392	0.3946
55.220	0.3989	0.5039	0.6114	0.7162	0.8169
59.821	0.7770	0.9777	1.1784	1.3659	1.5443
64.990	1.3567	1.7229	2.0799	2.4101	2.7034
69.929	2.0486	2.6645	3.2647	3.8336	4.3376
73.948	2.6051	3.4749	4.3401	5.1716	5.9117
74.910	2.6549	3.5500	4.4440	5.3075	6.0935
76.877	2.8373	3.8440	4.8543	5.8382	6.7132
77.532	2.8816	3.9066	4.9499	5.9482	6.8794
78.883	2.9731	4.0611	5.1759	6.2468	7.3942
79.490	2.9948	4.1030	5.2383	6.3422	7.3530
79.924	3.0134	4.1361	5.3060	6.4160	7.4508
80.081	3.0230	4.1524	5.3174	6.4462	7.4962
80.991	3.0542	4.2158	5.4108	6.5817	7.6672
82.015	3.0643	4.2415	5.4636	6.6647	7.7802
82.980	3.0613	4.2420	5.4831	6.7071	7.8546
83.903	3.0517	4.2381	5.4612	6.6744	7.8131
84.782	3.0205	4.2308	5.4548	6.6949	7.8580
85.916	2.9600	4.1181	5.3405	6.5502	7.7088
87.599	2.8200	3.9066	5.0625	6.2048	7.2892
89.880	2.5089	3.4458	4.4552	5.4733	6.4327
91.225	2.2263	3.0467	3.9190	4.7933	5.6421
93.848	1.4791	1.9928	2.5335	3.0720	3.5845
97.356			0.4706	0.5715	0.6793
100.000			$0.0_4 53$	$0.0_7 46$	$0.0_7 74$

MATERIALS

The pyridine and acetic acid used in these measurements were purified in the manner described in our previous paper (6). Conductivity water was prepared by redistillation of distilled water from acid potassium permanganate. A standard brand of C.P. potassium chloride, recrystallized from conductivity water and dried at 110°C. for twelve hours, was used for determining the cell constant.

METHOD

Mixtures covering the entire range of composition were made up by weight, with compositions expressed in mole per cent acetic acid.

The constancy of the cell characteristics was frequently checked during the conductance measurements. The cell plates were kept shorted at all times except while actual measurements were in progress, as recommended by Morgan and Lammert (2).

All bridge readings were taken as near the center of the bridge as possible.

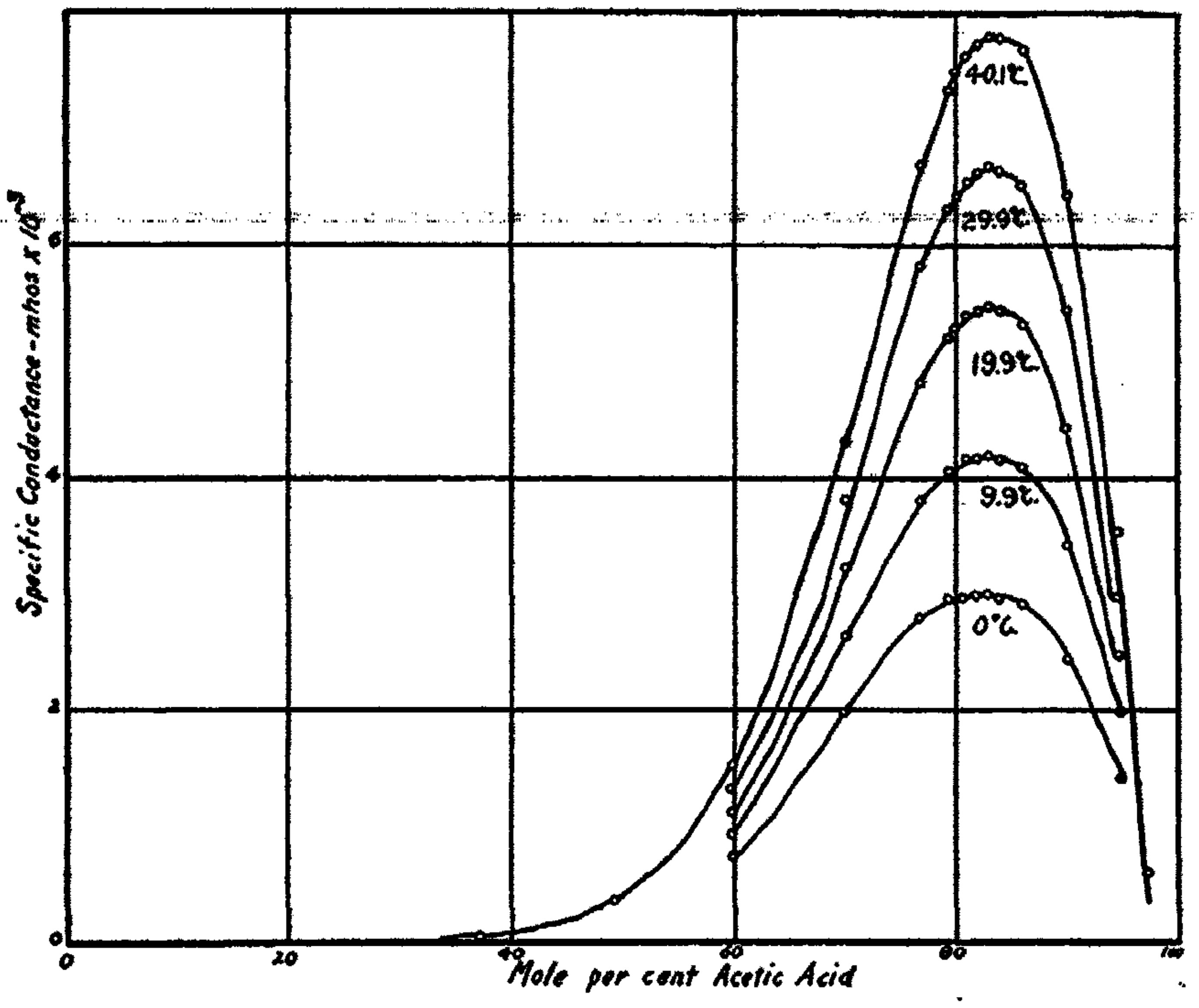

FIG. 1. SPECIFIC CONDUCTANCE ISOTHERMS FOR PYRIDINE-ACETIC ACID MIXTURES

Conductance measurements were made at 0, 9.9, 19.9, 29.9, and 40.1°C. These temperatures were maintained constant to within ±0.1°C.

EXPERIMENTAL RESULTS

Table I and figure 1 show the specific conductance of mixtures of pyridine and acetic acid over the entire range of composition for temperatures from 0°C. to 40.1°C. at approximately ten-degree intervals. The readings recorded are the average of several separate readings.

The specific conductance changes slightly, but regularly, with composition up to 50 mole per cent acetic acid. Above this composition, the specific conductance increases rapidly, reaching a pronounced maximum at about 83 mole per cent acetic acid. Beyond this concentration, the conductance drops rapidly to the low value for pure acetic acid. The position of the maximum remains practically constant over the temperature range investigated. The maximum is sharper at the higher temperatures.

There is no evidence of any irregularity in the specific conductance of this system at 50 mole per cent acetic acid, at which composition the melting point diagram indicates the existence of a complex. The sharp maximum in the conductance curve at 83 mole per cent acetic acid indicates, as do the viscosity and fusion point data, a complex of composition between 80 and 85 mole per cent acetic acid.

SUMMARY

The specific conductance of mixtures of pyridine and acetic acid has been measured over the entire range of composition.

The conductance data shows a single maximum at 83 mole per cent acetic acid, indicating a complex of this composition. This agrees with the viscosity data and in part with the melting point data for this system.

No evidence was obtained which would indicate the existence of a complex at 50 mole per cent acetic acid, as shown by the melting point data for this system.

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PHYSICOCHEMICAL STUDIES ON GUM ARABIC SOLUTIONS. III

Osmotic Pressures of Solutions of Arabic Acid and Sodium Arabate

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Received March 31, 1934

~~The manner in which diffusible ions will be found to be distributed at~~ equilibrium on the two sides of a membrane, on one side of which there exists a colloid electrolyte (one ion non-diffusible), has been placed on a theoretical foundation by Donnan (5, 6, 7), and the theory has been confirmed by him and by others in numerous experiments. Donnan's theory goes further, however, and predicts that the equilibrium osmotic pressure shown by such a system should be proportional to the difference between the total moles of diffusible ions inside and outside the membrane, modified by any osmotic effect arising from the colloid micellae.

For example, in a system containing only hydrochloric acid and arabic acid, HAr, where the colloid is contained inside of a membrane which is permeable to H^+ and Cl^- ions but not permeable to the arabate ion or to the arabic acid molecule, at equilibrium the diffusible ions will be distributed in such a manner that

$$[H^+]_i \cdot [Cl^-]_i = [H^+]_o \cdot [Cl^-]_o$$

and

$$\frac{[H^+]_i}{[H^+]_o} = \frac{[Cl^-]_o}{[Cl^-]_i}$$

Also,

$$[H^+]_o = [Cl^-]_o$$

but

$$[H^+]_i > [Cl^-]_i$$

(Here [H], [Cl] etc. must signify activities of the respective ions, but will be very nearly equal to their concentrations when very dilute solutions are employed.) These relationships have been experimentally shown to exist. The Donnan theory postulates, in addition, that the osmotic pressure which the solution inside the membrane will show, when in equilibrium with the solution outside, will be defined by the expression

$$\pi = RT\,[([\mathrm{H}^+]_i + [\mathrm{Cl}^-]_i + \Sigma\,[\mathrm{Micellae}]) - ([\mathrm{H}^+]_o + [\mathrm{Cl}^-]_o)]$$

This relationship, of course, would hold if the membrane were impermeable to all the dissolved substances but permeable to water. However, when the only restraining force acting to prevent movement of the diffusible ions across the membrane is the electrostatic attraction which has caused their unequal distribution, as in the example given, experiments, from time to time, have indicated that there exists a difference between the observed osmotic pressure and that calculated on the basis of the Donnan theory.

In fact, Donnan and Harris (8) and Bayliss (2) found for solutions of Congo red that the observed osmotic pressure was only 87 to 94 per cent of that calculated on the assumption of a molecularly dispersed but unionized state of the dye. Donnan assumed the formation of aggregates of dye molecules to explain this discrepancy between observed and calculated osmotic pressures. Zsigmondy (15) measured, in addition, the conductivity of the colloid solution and concluded that the relationship existing between conductivity and osmotic properties, even with the assumption of the formation of a large colloidal ion, could not be explained on the basis of the older theories. He postulated that the discrepancy arises as a result of interionic forces in the manner pictured by the Debye-Hückel theory.

Loeb (11) studied the osmotic pressures of solutions of various proteins and found that the difference in concentration in crystalloid ions on the two sides of the membrane, at equilibrium set up as a result of the Donnan phenomena, could account completely for the osmotic pressure shown by a solution of casein chloride (12). In this case the colloid micelle was apparently so large that it exerted no measurable osmotic pressure itself. With gelatin chloride Loeb found that the osmotic pressure observed did not coincide with that calculated from the difference in ionic concentrations, although it varied in much the same manner with change in pH of the system. Loeb believed that the osmotic properties of protein solutions were completely defined by the Donnan hypothesis.

More recently Rona and Weber (13) have measured the activities of the diffusible ions and the osmotic pressure at equilibrium in the system, myogen chloride + HCl. They found the ratio $[\mathrm{H}^+]_i/[\mathrm{H}^+]_o$ to be equal to the ratio $[\mathrm{Cl}^-]_o/[\mathrm{Cl}^-]_i$, but found deviations between observed and calculated osmotic pressures similar to those which Loeb found with gelatin solutions. At low concentrations of hydrochloric acid (near isoelectric point of the protein) the measured osmotic pressure was greater than that calculated on the basis of the measured diffusible ion distribution, while at higher hydrochloric acid concentrations the reverse was true. The former deviation was explained as due to the osmotic effect of the protein molecules themselves augmenting that of the diffusible ions. The latter deviation they picture as due to an influence of the large micellar ions exerted upon the osmotic activity of the small ions, which was noticeably different from (and greater than) their effect upon the electrode activity of the same ions.

E. Hammarsten (9) observed that the osmotic pressure exhibited by nucleic acid and Na_4-nucleate inside a collodion membrane, against distilled water on the outside, was less than that which the equilibrium distribution of small ions alone should show, also less than would be expected if no ionization occurred and the material were molecularly dispersed (calculated from the known molecular weight of the acid). He concluded, therefore, that some aggregation had taken place and that the small ions are active osmotically only to a small extent or not at all. This loss of osmotic activity of the small ions (which, however, still retain their activity at an electrode, since their concentrations were determined in this manner) he assumes to be due to an interionic influence resulting from the great difference in size of the colloid and crystalloid ions. In support of this explanation H. Hammarsten (10) found that the osmotic pressure of a solution of guanylic acid (ion of relatively small molecular weight) was that normally expected from the difference in total ionic concentration on the two sides of the membrane. (His calculations were made from the value of a maximum osmotic pressure observed after about six hours.) With salts of acids of higher molecular weight he confirmed the observations of E. Hammarsten. This anomalous osmotic effect, wherein the osmotic pressure of the colloid solution is less than would be calculated on the basis of the measured activities and distribution of the components present, has been called the "Hammarsten effect."

Bjerrum (3) measured the osmotic pressure, membrane potentials, and hydrogen-ion activity of solutions of chromium hydroxide and found that $P = P_1 + P_2$, where P was the observed pressure, P_1 was the osmotic pressure of the colloid particles (estimated to contain about one thousand chromium atoms), and P_2 was the osmotic pressure derived from the unequal distribution of ions on the two sides of the membrane. He found discrepancies between the observed membrane potentials and those calculated from osmotic pressure measurements, however, and believed this to be due to an unequal influence of the colloid upon the conductivity, electrode activity, and osmotic activity of ions adsorbed by it.

Samec, Knop, and Pankovic (14) measured osmotic pressures of an amylopectin (from potato starch), of lignosulfonic acid, and of an ammonium salt of humus (from peat) against water, using collodion sacs. They found the observed osmotic pressures to be less in all cases than would be expected from the measured difference in concentration of the small ions alone and to be of the order of magnitude to be expected from the molecular weights of the colloids, calculated from other data, entirely neglecting any ionization. Their conclusion was that the small ions (*Gegenionen*) were osmotically inactive. Samac and Ribaric, however, had found that the freezing point lowering in a lignosulfonic acid solution was very close to that required on the basis of hydrogen-ion concentration alone.

Adair (1) studied the osmotic pressure of hemoglobin against distilled water and against solutions of diffusible salts. He measured, at the same time, the membrane potentials and distribution of diffusible ions. His conclusions were (a) that the relationships between diffusible ion activities and membrane potentials were in accord with the Donnan theory, (b) that within a limited range of hydrion, salt, and protein concentrations the observed osmotic pressure was equal to the sum of the pressure derived from the colloid, molecularly dispersed, and the pressure arising as a result of unequal distribution of diffusible ions on the two sides of the membrane, and (c) that the theory of Barcroft and Hill, which pictures a variable degree of aggregation of the colloid in explanation of the anomalies observed in its osmotic pressure relationships, was not correct. Adair claims the large deviations from the van't Hoff law to result from changes in activity of the protein molecule, this being a function of salt concentration, hydrion concentration, and protein concentration.

Thus, while discrepancies between theory and experimental results have been repeatedly indicated, no adequate study has been made of the phenomenon. This is probably due to the fact that most of such work has been done with colloids, the micellar weight of which was sufficiently small so that the osmotic pressure arising therefrom could not be neglected. This complication makes it almost impossible to obtain accurate measures of the deviation of the calculated and observable osmotic effects of the diffusible ions alone. In the experiments described below, using purified, electrodialyzed gum arabic, the colloid micella was apparently so large as to exert negligible osmotic pressure, and the relationships existing between observed and calculated osmotic pressures arising from the unequal distribution of diffusible ions alone became relatively easily apparent.

EXPERIMENTAL

The method for preparation of the colloid, gum arabic, and some of its physical properties have been described in the first paper of this series (4). In the experiments described in the present paper, only the sodium salt of the arabic acid was used. This salt contained 85×10^{-6} equivalents of Na per gram of dry colloid. The electrodialyzed arabic acid was neutralized with sodium hydroxide and the solution evaporated to dryness *in vacuo* at

70°C. The colloid was kept in the dry form and the solutions were prepared as needed. This colloid has properties which are very desirable for this type of experiment. It has no isoelectric point, acting as an anion at all values of pH; it is infinitely soluble in water; it does not easily hydrolyze in acid solutions and it requires no preservative to prevent bacterial hydrolysis.

The method used for measuring the osmotic pressure of the solutions was that of applying a constant pressure to the colloid solution inside of a sac-shaped membrane which was partially or wholly immersed in an external solution containing no colloid, until equilibrium was attained throughout the system. Figure 1 shows diagrammatically the apparatus used. The samples of colloid to be examined (in duplicate) were placed in collodion sacs (E) which were fastened by rubber bands to the tube through which constant pressure was applied. The applied constant pressure was obtained by slowly and continuously forcing air into the system at T and allowing it to escape at B, thereby displacing water in the tube between B and the surface of the liquid external to the tube. The pressure effective on the meniscus of the colloid solution in E would then be equal to the

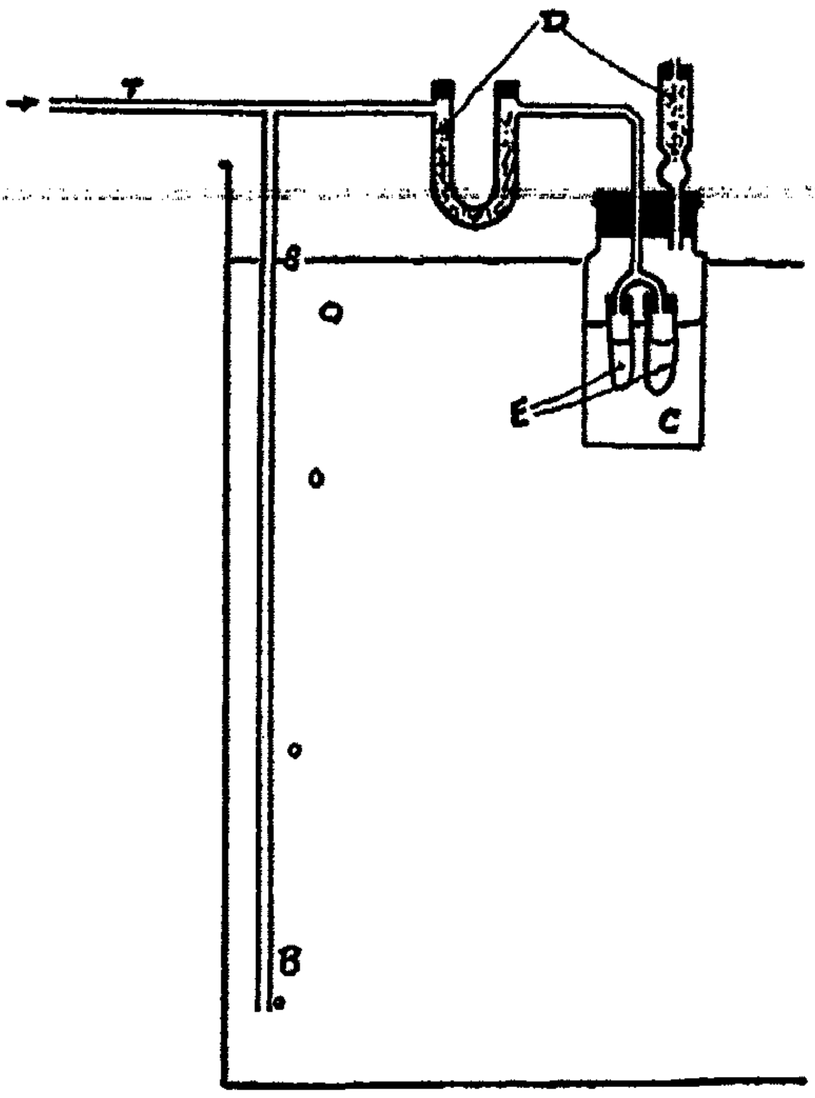

FIG. 1. DIAGRAMMATIC REPRESENTATION OF APPARATUS USED FOR OSMOTIC PRESSURE DETERMINATIONS

column of water displaced in the tube (S to B) modified by the difference in the height of the menisci in E and in C. Most of the experiments were carried out when the pH was well on the acid side of neutrality in order to eliminate carbon dioxide adsorption. In those cases where neutrality was approached in the solutions, carbon dioxide adsorption was reduced to a minimum by protecting both sides of the system containing the colloid and external solutions by soda lime tubes (D). This protection was imperfect, however, and in a few cases where the external solutions were nearly neutral it is necessary to assume that some bicarbonate ion is present.

The final volume containing the colloid was determined by weighing the solution left inside the membrane at equilibrium. The observed (equilibrium) osmotic pressure, then, would be equal to the constant pressure applied. The final concentration of the colloid in solution could be calculated from the amount of colloid initially placed in the sac and its volume as determined from the final weight of the solution. The final volumes (V_i) used for the colloid solutions in the following tables of calculations are corrected for the weight of gum arabic present in each instance (i.e., $V_i = F - A$). V_i, therefore, signifies the volume of solvent left inside the membrane at equilibrium. The membranes used were made of collodion. They were prepared in the usual manner, no particular care being exercised as to uniformity of their preparation. The only care taken in their preparation was that required to get them thick enough to withstand the pressure applied and to prevent leaks, but not so thick or impermeable as to require too long a time for equilibrium to be reached. Equilibrium values obtained are independent of the pore radius and material of the membrane.

In all experiments the determinations were made in duplicate by placing equal amounts of colloid in two sacs which were then placed under the same pressure with a common external solution. A criterion for the attainment of equilibrium was as follows: Two equal samples of the colloid were weighed out and placed in the two collodion sacs. To one was added 10 cc. of distilled water. Both were then placed in the same external solution under the same pressure and allowed to stand. After about forty-eight hours the weights of solution inside of each sac had reached identical values. Since water moved out of one sac and was drawn into the other to reach the same final amount in each, this final value was a true equilibrium value. In all the experiments at least sixty hours were allowed for equilibrium to be attained.

In the tables the final weight of solution in each sac is given in the column designated by F; the weight of dry colloid contained in each is given in the column under A. Subsequent measurements of pH and all calculations are made upon the combined samples. In all experiments, except those given in table 1, the measurements were carried out in individual 500-cc. bottles, as shown in figure 2.

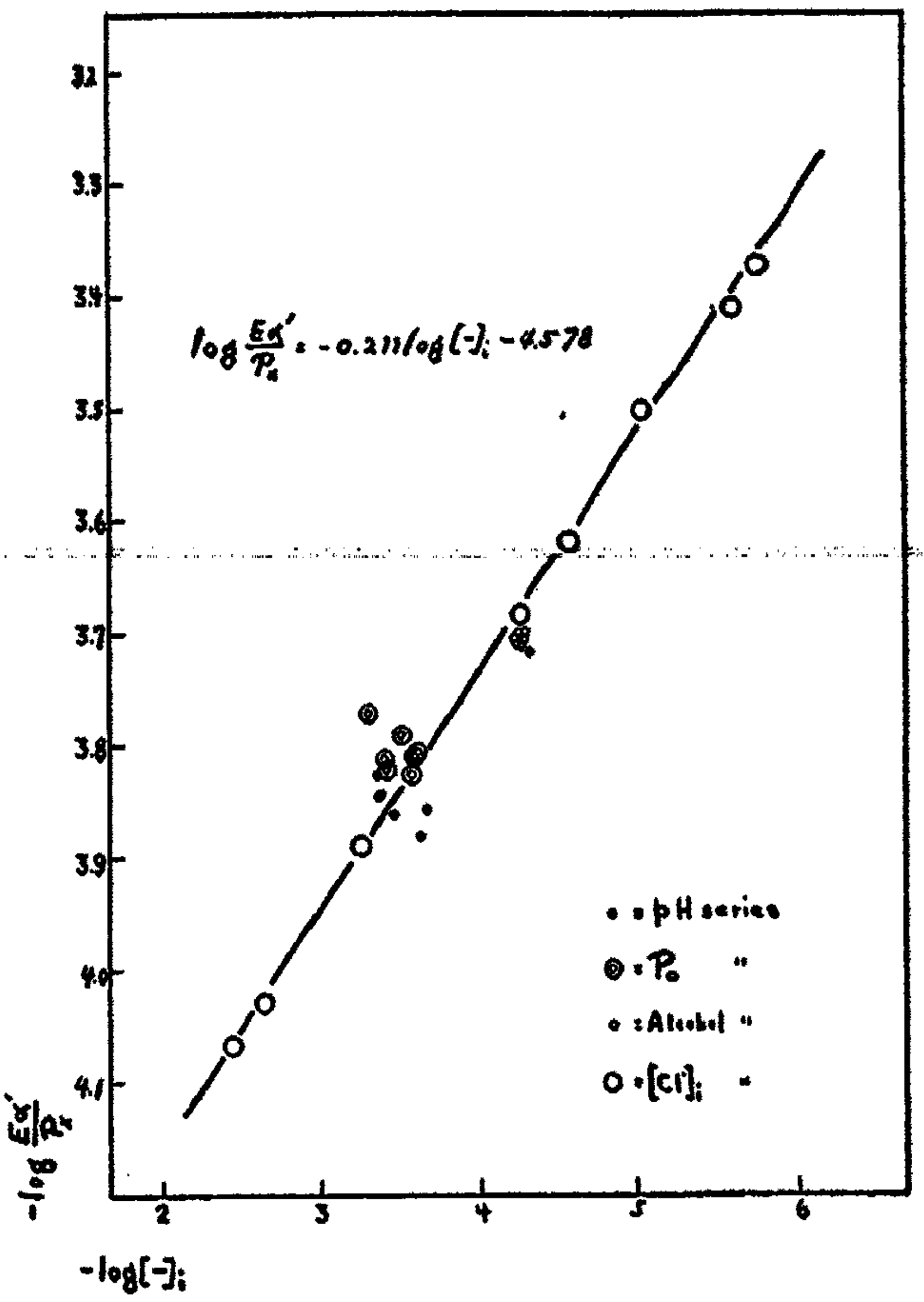

FIG. 2. GRAPH SHOWING THE MANNER IN WHICH THE FACTOR $E\alpha'/P_x$ VARIES WITH CHANGE IN CONCENTRATION OF FOREIGN SALT, $[-]_i$, IN THE COLLOID SOLUTION

E = the potential across the membrane which is impermeable to the colloid ion; α' = the number of equivalents of ions derived from one gram of the colloid; and $P_x = P_c - P_o$ is a measure of the deviation of the osmotic pressure calculated according to the Donnan hypothesis, P_c, from the observed equilibrium osmotic pressure, P_o, across the membrane. $[-]_i$ signifies the concentration of anions other than the colloid anion within the colloid-containing solution.

The volumes of solvent present in the internal (i) and external (o) solutions, at equilibrium, are given in the tables in the column designated as V, and the pressure against which equilibrium was attained, by P_0. All experiments were made at 25°C.

After equilibrium had been gained, the hydrogen-ion concentration was determined electrometrically (with the hydrogen electrode) on the inside and outside solutions. These measurements gave directly the difference in potential, E (millivolts), across the membrane, and from this could be calculated the ratio of distribution of hydrogen ions in the system. This ratio is shown in the tables as R. $R = \text{antilog}\,(E/59.1)$.

The total equivalents of Na and Cl present in the system in each case are shown in the tables under columns headed by "Na" and "Cl," respectively. Since, according to Donnan's membrane equilibrium theory,

$$\frac{[\mathrm{H^+}]_i}{[\mathrm{H^+}]_o} = \frac{[\mathrm{Na^+}]_i}{[\mathrm{Na^+}]_o} = \frac{[\mathrm{Cl^-}]_o}{[\mathrm{Cl^-}]_i} = R$$

this value of R together with a knowledge of the volumes, V, inside and outside, and the total equivalents of each species of anion or cation present in the system, makes it possible to calculate the actual concentrations of each on both sides of the membrane. These values have been calculated assuming 100 per cent activity in all cases except where definitely indicated otherwise. The equilibrium concentrations of the various diffusible ions on the two sides of the membrane were calculated according to equations such as

$$[\mathrm{Na^+}]_o = \frac{\text{Total Na (equiv.)}}{(R \cdot V_{i/1000}) + V_{o/1000}},\ [\mathrm{Na^+}]_i = R \cdot [\mathrm{Na^+}]_o$$

$$[\mathrm{Cl^-}]_i = \frac{\text{Total Cl (equiv.)}}{(R \cdot V_{o/1000}) + V_{i/1000}},\ [\mathrm{Cl^-}]_o = R \cdot [\mathrm{Cl^-}]_i$$

where V_i and V_o = equilibrium volumes of solvent in cubic centimeters inside and outside, respectively.

The electrolyte concentration in all cases where 100 per cent ionization is assumed is of such a low order that the error so introduced is very small. In the tables, the concentrations of these ions are given under the heading $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{H^+}]$, etc. and signify the concentration in equivalents per liter multiplied by 10^7. If the Donnan equilibrium theory holds in these cases, the total concentration of the positive ions should equal that of the total negative ions in the outside solution, where diffusible electrolytes alone are present. In the majority of cases this agreement is very close, and the conclusion is that the ions distribute themselves in accordance with the membrane equilibrium theory.

Knowing, now, the actual concentration (activities) of all ions on both sides of the membrane (neglecting, for the present, the colloid ion, since its molecular weight is high and unknown), the difference $[D]$, between their totals, $[T]$, inside and outside, will be a measure of the difference in their osmotic concentrations across the membrane. At 25°C. 1 mole of dissolved material exerts an osmotic pressure equal to 25280 cm. of water. Then, $[D] \times 25280 \times 10^{-7}$ gives the effective osmotic pressure, P_c, in centimeters of water, exerted by the ions, assuming that the large colloid ion itself exerts no appreciable osmotic pressure and that it does not influence the osmotic activity of the small ions to a degree differing from its influence on the activity of these ions as determined electrometrically (i.e., from hydrogen-ion activity measured electrometrically and values calculated therefrom in the above outlined manner).

Examination of the tables reveals that in all cases the values of P_c are greater than the corresponding values of P_o, that is, the calculated osmotic pressure arising from the unequal distribution of the small ions alone is greater than the observed osmotic pressure. This is in accord with observations referred to above in the cases of certain other colloid solutions. Any osmotic pressure arising from the colloid ion itself would be in a direction such as to increase this difference. The value, $P_c - P_o = P_x$, is a measure of an anomalous equilibrium osmotic pressure of the colloid-containing system (continuing to neglect any possible osmotic pressure derived from the colloid itself).

In the experiment shown in table 1, the vessel used to contain the external solution was a tall glass cylinder. The external solution was common to all the sacs. Pressure was varied by placing the sacs at different levels below the surface of the liquid and applying an equal external pressure to all. The effective pressure then would be the difference between the applied pressure and the counter pressure exerted by the depths of water above the meniscus of the colloid solution in the sac, i.e., the weight of a column of water equal to the distance of this meniscus below the surface of the liquid in the containing cylinder.

For table 2 the variable was the pH. The total Cl content was kept constant in all the experiments and the pH varied individually by varying the relative amounts of NaCl and HCl added. In this case, and in all those in succeeding tables, the value of P_o was held nearly constant.

In the experiments shown in table 3, all variables were held constant except ethyl alcohol content, which was varied from 0.25×10^{-3} molar to 0.25 molar. This experiment was made in order to find out if diffusible non-electrolytes had any effect upon the osmotic properties of the colloid solution. These results serve, perhaps, to show the extremes of error in the determinations and in the calculated value of P_c. This is of the order of 10 per cent, the presence of the alcohol apparently having no effect upon the equilibrium attained.

Table 4 shows results obtained when the total Cl was changed from zero to 0.01 normal solution. In this case a mixture of 5 parts NaCl and 1 part HCl was added to the individual experiments in varying amounts so as to change the total Cl. The hydrochloric acid was added in order to

TABLE 1

Pressure varying; same external solution

NO.	SIDE OF MEMBRANE	IN TOTAL SOLUTION = 3000 cc. (i + o)		A	F	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_x$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_x} \times 10^4$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^7$										
		equiv. $\times 10^3$	*equiv.* $\times 10^3$	*grams*	*grams*	*cc.*	*cm.* H_2O	*mv.*			*mv.*						*cm.* H_2O	*cm.* H_2O		
1	i	4.513	2.550	0.100 0.100	5.201 5.029	10.030	14.5	405.8	2.722	18960	23.9	2.530	20050	6050	45060	14331	36.3	21.8	1.653	1.813
2	i	4.513	2.550	0.100 0.100	3.829 3.848	7.477	27.3	401.0	2.639	22950	28.7	3.061	24260	5000	52210	21481	54.2	26.9	1.577	1.682
3	i	4.513	2.550	0.150 0.150	4.865 4.840	9.405	37.8	397.3	2.578	26420	32.4	3.525	27930	4343	58693	27964	70.7	32.9	1.568	1.542
4	i	4.513	2.550	0.150 0.150	3.965 4.245	7.910	48.7	395.0	2.540	28830	34.7	3.847	30490	3980	63300	32571	82.4	33.7	1.460	1.520
5	i	4.513	2.550	0.200 0.200	3.850 3.836	7.296	85.7	389.4	2.443	36050	40.3	4.810	38110	3184	77344	46615	117.8	32.1	1.294	1.622
6	i	4.513	2.550	0.200 0.200	3.534 3.518	6.652	97.4	387.1	2.404	39430	42.6	5.260	41700	2914	84044	53315	134.8	37.4	1.302	1.482
7	i	4.513	2.550	0.300 0.300	4.961 4.915	9.276	110.5	385.5	2.377	41960	44.2	5.595	44350	2735	89045	58316	147.5	37.0	1.291	1.542
8	i	4.513	2.550	0.300 0.300	4.673 4.784	8.857	119.5	384.4	2.358	43830	45.3	5.850	46360	2617	92807	62078	157.1	37.6	1.292	1.567
	out					2933.1		429.7	3.125	7495			7924	15310	30729					

Legend for the tables: A = grams of arabate in sample. F = final weight of solution containing sample inside of membrane. V = volume of water at equilibrium on each side of membrane (in cc.). P_o = observed (or equilibrium) osmotic pressure (in cm. of water). $[H^+]$, $[Na^+]$, etc. = final concentration of diffusible ions (in equivalents per liter $\times 10^7$). E = membrane potential = $59.1 \times (pH_o - pH_i)$ (in millivolts). R = *ratio of distribution of diffusible ions.* $[T]$ = total concentration of diffusible ions (in equivalents per liter $\times 10^7$) on each side of membrane. $[D]$ = difference in concentration of diffusible ions (in equivalents per liter $\times 10^7$) across membrane. P_c = calculated osmotic pressure = $(D) \times 25280 \times 10^{-7}$ (in cm. of water). $P_x = P_c - P_o$. α' = equivalents ($\times 10^7$) of ions derived from 1 g. of colloid. $[-]_i = [Cl^-]_i + [HCO_3^-]_i$ (in equivalents per liter).

TABLE 2

Varying pH; total [Cl] constant; pressure constant

NO.	SIDE OF MEMBRANE	IN 320 CC. = TOTAL VOLUME OF SOLUTION (i + o)		A	F	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_x$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_x} \times 10^4$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^7$										
		equiv. $\times 10^3$	*equiv.* $\times 10^3$	*grams*	*grams*	*cc.*	*cm.* H_2O	*mv.*			*mv.*						*cm.* H_2O	*cm.* H_2O		
1	i	0.680	0.340	0.200 0.200	2.589 2.583	4.77	127.1	379.4	2.273	53320	39.6	4.696	47320	4580	105220	62370	157.5	30.4	1.146	1.492
	o					314.83		419.0	2.945	11350			10080	21520	42850					
2	i	0.680	0.437	0.200 0.200	2.860 2.884	5.37	127.1	385.4	2.375	42170	40.1	4.786	61520	4505	108195	64955	164.2	37.1	1.331	1.440
	o					314.23		425.5	3.055	8810			12860	21520	43240					
3	i	0.680	0.534	0.200 0.200	3.161 3.235	6.00	127.6	393.8	2.519	30280	40.9	4.910	76400	4398	111078	67748	171.2	43.6	1.535	1.440
	o					313.60		434.7	3.210	6165			15565	21600	43330					
4	i	0.680	0.631	0.200 0.200	3.735 3.734	7.07	127.5	405.0	2.707	19630	42.0	5.166	93400	4191	117221	73691	186.2	58.7	1.922	1.377
	o					312.53		447.0	3.420	3800			18080	21650	43530					
5	i	0.680	0.728	0.200 0.200	4.567 4.742	8.91	128.1	422.5	3.003	9930	43.3	5.392	109470	4039	123439	79528	201.0	72.9	2.570	1.526
	o					310.69		465.8	3.735	1841			20300	21770	43911					
6	i	0.680	0.826	0.200 0.200	5.488 5.403	10.49	128.8	445.5	3.391	4062	46.5	6.150	136000	3558	143620	98970	250.0	121.2	3.580	1.375
	o					309.11		492.0	4.180	660.5			22110	21880	44650					
7	i	0.680	0.923	0.200 0.200	6.495 6.520	12.62	129.5	483.1	4.030	933.0	55.9	8.810	194500	2503	197936	153700	388.3	258.8	6.090	1.317
	o					306.98		539.0	4.975	105.9			22060	22070	44236					
8	i	0.680	0.1020	0.200 0.200	7.288 7.272	14.16	129.0	587.4	5.793	16.10	59.2	10.08	229500	2200	231700	186770	472.0	343.0	8.050	1.392
	o					305.44		646.6	6.797	1.596			22750	22180	44930					

TABLE 3

Alcohol varying; [Cl] constant; pressure constant; [Na] constant

NO.	SIDE OF MEMBRANE	IN 320 CC. = TOTAL VOLUME OF SOLUTION (i + o)		$[C_2H_5OH] \times 10^3$	A	P	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_x$	$a' \times 10^4$	$\frac{Ea'}{P_x} \times 10^4$
		Cl	Na						E.M.F.	pH	$[H^+] \times 10^7$										
		equiv. × 10³	*equiv.* × 10³		*grams*	*grams*	*cc.*	*cm.* H_2O	*mv.*			*mv.*						*cm.* H_2O	*cm.* H_2O		
1	i	0.3128	0.5930	0.25	0.200 0.200	8.380 8.382	16.36	130.2	511.3	4.505	312.5	75.0	18.52	181300	555.5	182200	162100	410.0	279.8	7.41	1.987
	o						303.2		586.3	5.773	16.86			9790	10280	20100					
2	i	0.3128	0.5930	0.50	0.200 0.200	8.449 8.410	16.46	130.2	512.7	4.530	295.0	73.6	17.50	175500	587.0	176400	155800	394.0	263.8	7.21	2.010
	o						303.1		586.3	5.773	16.86			10300	10280	20600					
3	i	0.3128	0.5930	5.00	0.200 0.200	8.353 8.288	16.24	129.8	510.8	4.500	316.2	72.5	16.80	172800	611.0	173700	153100	387.0	257.2	7.00	1.974
	o						303.4		583.3	5.725	18.82			10295	10270	20600					
4	i	0.3128	0.5930	10.00	0.200 0.200	8.388 8.356	16.34	130.2	509.4	4.475	335.0	74.9	18.76	182400	548.0	183300	163300	413.0	282.8	7.43	1.971
	o						303.3		584.8	5.748	17.86			9725	10290	20000					
5	i	0.3128	0.5930	25.00	0.200 0.200	8.442 8.370	16.41	130.2	511.1	4.502	314.7	75.2	18.66	181500	551.0	182400	162400	410.5	280.3	7.43	1.995
	o						303.2		586.3	5.773	16.86			9730	10280	20000					
6	i	0.3128	0.5930	50.00	0.200 0.200	8.359 8.273	16.23	129.9	510.9	4.500	316.2	73.7	16.95	173750	607.0	174700	154200	390.0	260.1	7.04	1.995
	o						303.4		583.6	5.730	18.65			10250	10280	20500					
7	i	0.3128	0.5930	250.00	0.200 0.200	8.519 8.504	16.68	127.2	513.9	4.549	282.3	74.6	18.23	178100	565.0	178900	158800	401.5	274.3	7.42	2.018
	o						302.9		588.5	5.810	15.48			9770	10300	20100					
8	i	0.3128	0.5930	800.00	0.200 0.200	8.224 8.194	16.14	127.6	511.1	4.502	314.7	77.6	20.54	192700	501.0	193500	173900	439.6	312.0	7.77	1.930
	o						303.8		588.7	5.815	15.31			9340	10270	19600					

TABLE 4

[Cl] varying; pressure constant

NO.	SIDE OF MEMBRANE	IN 320 CC. = TOTAL SOLUTION (i + o)					A	P	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[HCO_3^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_t$	$a' \times 10^4$	$\frac{Ea'}{P_t} \times 10^4$	$-\log \frac{Ea'}{P_t}$	$-\log [-]_i$	$[-]_i^{0.211}$	$\frac{Ea' [-]_i^{0.211}}{P_t} \times 10^3$
		Cl	Activity coefficient of NaCl γ	$\gamma \times$ Cl	Na	$\gamma \times$ Na					E.M.F.	pH	$[H^+] \times 10^7$															
		equiv. $\times 10^3$		*equiv.* $\times 10^3$	*equiv.* $\times 10^3$	*equiv.* $\times 10^3$	*grams*	*grams*	*cc.*	*cm.* H_2O	*mv.*			*mv.*							*cm.* H_2O	*cm.* H_2O						
1	i				0.2550	0.2550	0.150	8.207	16.142	131.5	558.6	5.305	49.52	114.4	86.50	129800		17.4	129865	126865	320.5	189.0	6.99	4.230	3.374	5.759	0.06240	2.640
	o						0.150	8.235	303.56		673.0	7.242	0.5725			1500		1500	3000									
2	i	0.032	0.993	0.0318	0.2817	0.2796	0.150	8.137	15.962	130.8	552.7	5.206	62.20	111.0	75.15	139800	13.34	11.45	139887	136163	344.1	213.3	7.44	3.880	3.411	5.605	0.06645	2.580
	o						0.150	8.125	303.74		663.7	7.082	0.8275			1861	1003	860	3724									
3	i	0.096	0.988	0.0948	0.3350	0.3310	0.150	7.669	14.970	131.5	548.2	5.130	74.10	94.8	39.90	146300	77.0	14.1	146460	139120	351.5	220.0	7.30	3.140	3.500	5.036	0.08750	2.754
	o						0.150	7.601	304.73		643.0	6.731	1.857			3670	3110	560	7340									
4	i	0.224	0.983	0.2202	0.4841	0.4760	0.175	8.089	15.703	131.2	526.2	4.767	171.0	81.5	23.40	165950	309		166340	152020	381.9	250.7	7.45	2.421	3.616	4.510	0.11280	2.733
	o						0.175	7.964	303.95		607.7	6.136	7.310			7090	7230		14320									
5	i	0.320	0.977	0.3128	0.6066	0.5930	0.200	8.626	16.804	131.0	518.2	4.629	235.0	74.4	18.12	177000	568		177800	157720	398.5	267.5	7.42	2.065	3.685	4.245	0.12820	2.646
	o						0.200	8.578	302.80		593.0	5.887	12.97			9770	10300		20080									
6	i	0.960	0.960	0.9220	1.1825	1.1360	0.225	6.450	12.499	130.4	464.8	3.720	1905.0	43.2	5.373	163200	5540		170650	110170	278.4	148.0	4.44	1.295	3.887	3.246	0.20800	2.692
	o						0.225	6.493	307.05		508.0	4.450	354.7			30360	29770		60480									
7	i	2.240	0.936	2.0970	2.3760	2.2240	0.300	5.401	10.168	130.4	429.2	3.115	7672.0	27.2	2.898	190400	23130		221200	85820	217.0	86.6	2.97	0.932	4.031	2.636	0.27920	2.602
	o						0.300	5.367	309.23		456.4	3.577	2648.0			65680	67050		135380									
8	i	3.200	0.922	2.9500	3.2610	3.0080	0.350	5.077	9.344	130.1	417.6	2.920	12020.0	22.2	2.378	215300	39530		266850	77200	195.2	65.1	2.51	0.854	4.068	2.403	0.31260	2.670
	o						0.350	4.967	309.96		439.8	3.296	5056.0			90600	94000		189650									

keep the pH on the acid side of neutrality and minimize carbon dioxide absorption. In this table the activity coefficients of sodium chloride were used to calculate the active concentration of Na^+ and Cl^- ions present, i.e., 100 per cent activity was not assumed. This use of the activity coefficients of sodium chloride is not entirely correct (not all the electrolyte was sodium chloride), but serves to give a somewhat closer approximation to the actual conditions than if 100 per cent activity were assumed. While not shown in the table, the chloride ion concentrations were determined electrometrically with the silver-silver chloride electrode in the external solution and were found to agree closely with the calculated values given. The agreement for the inside solutions was not good, especially at low chloride concentrations, the electrode measurements indicating concentrations which were somewhat higher than the calculated values given in the table. This was probably due to a fault in the electrode, since others have found the $[H^+]_i/[H^+]_o$ ratio to equal the $Cl[^-]_o/[Cl^-]_i$ ratio as required by the Donnan theory.

Analysis of these data shows, empirically, that the factor $E\alpha'/P_x$ is essentially a constant in those cases (tables 1, 2, and 3) in which the foreign salt concentration (as measured in terms of $[-]_i$, the total negative ion concentration inside the membrane other than the colloid ion itself) does not vary radically. The factor E is the membrane potential as obtained from the pH measurements, and $P_x = P_c - P_o$ and is a measure of the anomalous pressure found. The factor, α', signifies the equivalents of sodium and hydrogen derived from one gram of the colloid. The final gram concentration of the colloid being equal in each case to $A/V_i \cdot 1000$ and the equivalent concentration of the ions derived from the colloid being equal to $[H^+]_i + [Na^+]_i - [Cl^-]_i$, the volume of α' is given by the equation

$$\alpha' = \frac{[H^+]_i + [Na^+]_i - [Cl^-]_i}{A/V_i \cdot 1000}$$

When, however, the foreign salt concentration, $[-]_i$, is changed radically, as in table 4, the value $E\alpha'/P_x$ is no longer a constant. Figure 2 shows that the value $E\alpha'/P_x$ varies with the factor $[-]_i$ in a log-log ratio. Graphic solution of the curve so obtained gives the equation

$$\log \frac{E\alpha'}{P_x} = -0.211 \log [-]_i - 4.578$$

Thus it appears that the value

$$\frac{E\alpha'[-]_i^{0.211}}{P_x}$$

is a constant when, other than the colloid, only monovalent cations and anions are present in the system. This factor does not vary with concentration of colloid, salt, or pH.

SUMMARY

A method is outlined by which accurate osmotic pressure concentration relationships may be obtained for systems containing a colloid as the non-diffusible component.

Osmotic pressure measurements made on solutions containing arabic acid and sodium arabate show that the equilibrium distribution of water and diffusible ions across the membrane is independent of the size of pore and of the material of the membrane.

The equilibrium distribution of diffusible ions across the membrane is in accord with the Donnan membrane equilibrium theory.

The osmotic pressure, *calculated* on the basis of unequal distribution of diffusible ions and the Donnan theory, is consistently greater than the *observed* equilibrium pressure.

The difference between the observed and calculated osmotic pressures ($P_c - P_o = P_x$) bears a definite relationship to certain other variables in the system such that

$$\frac{E\alpha'[-]_i^{0.311}}{P_x} = \text{constant}$$

This factor remains constant through all changes in pH, sodium chloride concentration, and colloid concentration in the system. In this factor, obtained empirically, E represents the potential existing at equilibrium across the membrane, α' is a measure of the number of equivalents of small diffusible ions (*Gegenionen*) derived from unit weight of the colloid, and $[-]_i$ is a measure of the concentration of salt inside the membrane other than the colloid itself.

Diffusible non-electrolytes (ethyl alcohol), in concentrations up to 0.5 molar solution, exert no influence upon this relationship.

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ACTIVITY COEFFICIENTS IN MIXED SOLUTIONS AND THE GIBBS-DUHEM AND DUHEM-MARGULES FORMULAS

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Received April 26, 1934

For a one-phase system consisting of a solvent (component 1) and $(x-1)$ solute species (components $2, 3 \ldots x$) the so-called Gibbs-Duhem formula would commonly be written as follows:

$$\sum_{i=1}^{i=x} n_i \cdot \mathrm{d}\mu_i = 0 \tag{1}$$

n_i is the number of moles of constituent i, μ_i the chemical potential of that constituent. Equation 1 is a particular case of the more general thermodynamic relation:

$$-S \cdot \mathrm{d}T + V \cdot \mathrm{d}P - \sum_i n_i \cdot \mathrm{d}\mu_i = 0 \tag{2}$$

where the symbols S, T, V, P have their usual meaning. Equation 1 rules any variation of composition taking place at constant pressure and temperature. The proof of the Gibbs-Duhem formula is based upon the fact that the dependence of the chemical potentials μ_i (like that of all partial molar quantities) on composition only involves the mole fractions of the various constituents. In other words the various μ_i's are homogeneous and of degree zero in terms of the n_i's. Euler's theorem on homogeneous functions gives then, for the chemical potential μ_i (1, 7)

$$\sum_{j=1}^{j=x} n_j \frac{\partial \mu_i}{\partial n_j} = 0 \tag{2}$$

There are x relations of this type ($i = 1, 2, \ldots x$). The partial derivatives are taken at T, P, and all n_i's except n_j, constant. Applying now the well-known reciprocity relations:

$$\frac{\partial \mu_i}{\partial n_j} = \frac{\partial \mu_j}{\partial n_i} = \frac{\partial^2 F}{\partial n_i \partial n_j} \tag{3}$$

F being the free energy of the system, we may transform the set of equations 2 into the equivalent set of x equations:

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \mu_j}{\partial n_i} = 0 \tag{4}$$

In the particular case of two constituents the set 2 becomes:

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_1} + n_2 \cdot \frac{\partial \mu_1}{\partial n_2} = 0 \tag{2.1}$$

$$n_1 \cdot \frac{\partial \mu_2}{\partial n_1} + n_2 \cdot \frac{\partial \mu_2}{\partial n_2} = 0 \tag{2.2}$$

The reciprocity relations 3 reduce to:

$$\frac{\partial \mu_1}{\partial n_2} = \frac{\partial \mu_2}{\partial n_1} \tag{3.1}$$

and the set 4 becomes:

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_1} + n_2 \cdot \frac{\partial \mu_2}{\partial n_1} = 0 \tag{4.1}$$

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_2} + n_2 \cdot \frac{\partial \mu_2}{\partial n_2} = 0 \tag{4.2}$$

We thus have as many equations of the Gibbs-Duhem type as there are components. These equations assume the form 2 or the form 4. Each set contains a total number of x^2 partial derivatives of the type $\frac{\partial \mu_i}{\partial n_j}$. The chemical potentials μ_i are of the form (1, 2)

$$\mu_i = \mu_i^0(T, P) + RT \cdot \log N_i f_i \tag{5}$$

μ_i^0 is a function of T and P only, R is the molar gas constant, N_i is the mole fraction and f_i the activity coefficient of the constituent i. We have (writing $\Sigma n_i = n$):

$$\frac{\partial \mu_i}{\partial n_i} = \frac{RT}{N_i} \cdot \frac{n - n_i}{n^2} + RT \cdot \frac{\partial \log f_i}{\partial n_i} \tag{6.1}$$

$$\frac{\partial \mu_i}{\partial n_j} = \frac{RT}{N_i} \cdot \frac{-n_i}{n^2} + RT \cdot \frac{\partial \log f_i}{\partial n_j} \tag{6.2}$$

The sets of equations 2 and 4 thus become:

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \log f_i}{\partial n_j} = 0 \qquad (i = 1, 2, \cdots x) \tag{7}$$

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \log f_j}{\partial n_i} = 0 \qquad (i = 1, 2, \cdots x) \tag{8}$$

In the particular case of two components these equations become:

$$n_1 \frac{\partial \log f_1}{\partial n_1} + n_2 \frac{\partial \log f_1}{\partial n_2} = 0 \tag{7.1}$$

$$n_1 \frac{\partial \log f_2}{\partial n_1} + n_2 \frac{\partial \log f_2}{\partial n_2} = 0 \tag{7.2}$$

and

$$n_1 \cdot \frac{\partial \log f_1}{\partial n_1} + n_2 \cdot \frac{\partial \log f_2}{\partial n_1} = 0 \tag{8.1}$$

$$n_1 \cdot \frac{\partial \log f_1}{\partial n_2} + n_2 \cdot \frac{\partial \log f_2}{\partial n_2} = 0 \tag{8.2}$$

The reciprocity relations 3 lead to analogous relations between the activity coefficients:

$$\frac{\partial \log f_i}{\partial n_j} = \frac{\partial \log f_j}{\partial n_i} \tag{9}$$

For a two-component system:

$$\frac{\partial \log f_1}{\partial n_2} = \frac{\partial \log f_2}{\partial n_1} \tag{9.1}$$

Besides the equations 7 or 8 we have the reciprocity relations 9 between the x^2 partial derivatives $\frac{\partial \log f_i}{\partial n_j}$. The number of distinct reciprocity relations is $\frac{x(x-1)}{2}$. (One differentiates each $\log f_i$ with respect to all the n_j's except n_i; each of the corresponding relations appears twice in the list.)

The total number of relations between the x^2 partial derivatives is thus:

$$x + \frac{x(x-1)}{2} = \frac{x(x+1)}{2} \tag{10}$$

In order to know all the partial derivatives in terms of all the n_i's we need

$$x^2 - \frac{x(x+1)}{2} = \frac{x(x-1)}{2} \tag{11}$$

non-thermodynamic relations. (Relations obtained in non-thermodynamic theories such as that of electrolytes; empirical relations deduced from experimental data.) When all the $\frac{\partial \log f_i}{\partial n_j}$ of constituent i are known in terms of the various n_j's the total differential of $\log f_i$

$$d \log f_i = \sum_{j=1}^{j=z} \frac{\partial \log f_i}{\partial n_j} \cdot dn_j \tag{15}$$

is known.

Formula 15 is an exact differential since, on account of the reciprocity relations 9,

$$\frac{\partial^2 \log f_i}{\partial n_k \cdot \partial n_j} = \frac{\partial^2 \log f_j}{\partial n_k \cdot \partial n_i} \tag{16}$$

or

$$\frac{\partial}{\partial n_k}\left(\frac{\partial \log f_i}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial \log f_i}{\partial n_k}\right) \tag{17}$$

$\log f_i$ is then obtained by means of quadratures:

$$\log f_i = \varphi_i(n_1 \cdots n_j \cdots n_z) + \text{Constant} \tag{18}$$

The constant is determined by making a suitable assumption concerning a particular composition of the solution; for instance one assumes that $f_i = 1$ at infinite dilution (all n_j's, except n_1, equal to zero).

Attempts in the literature (5, 6, 7) to introduce the mole fractions N_i instead of the numbers of moles n_i in formulas 2 and 4 or in 7 and 8 have often led to incorrect equations. Dividing formulas 2 and 4 by n we obtain:

$$\sum_{j=1}^{j=z} N_j \cdot \frac{\partial \mu_i}{\partial n_j} = 0 \tag{19}$$

$$\sum_{j=1}^{j=z} N_j \cdot \frac{\partial \mu_j}{\partial n_i} = 0 \tag{20}$$

Formula 20 is often incorrectly written:

$$\sum_{j=1}^{j=z} N_j \cdot \frac{\partial \mu_j}{\partial N_i} = 0 \tag{21}$$

For the particular case of a two-component system formula 21 becomes:

$$N_1 \cdot \frac{\partial \mu_1}{\partial N_1} + N_2 \cdot \frac{\partial \mu_2}{\partial N_1} = 0 \tag{22}$$

It is however obvious, if one refers to equation 1, that the correct way of writing 22 is

$$N_1 \cdot \frac{d\mu_1}{dN_1} + N_2 \cdot \frac{d\mu_2}{dN_1} = 0 \tag{23}$$

and in general:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{d\mu_j}{dN_i} = 0 \tag{24}$$

Formula 24 could be considered as the correct general form of the Duhem-Margules formula. For ideal systems it reduces to an identity. For non-ideal systems it becomes:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{d \log f_j}{dN_i} = 0 \tag{25}$$

The confusion between formulas 22 and 23 has already been pointed out by Lecat (4).

Example 1. If $x = 2$ we need one non-thermodynamic relation: for instance, the dependence of $\log f_1$ or of the osmotic coefficient of the solvent on composition, as deduced from freezing point data. Such data will usually give $\frac{\partial \log f_1}{\partial n_2}$. Introducing the osmotic coefficient g_1, we make use of the relation:

$$\log f_1 = (g_1 - 1) \cdot \log N_1 \tag{26}$$

Differentiating with respect to n_2:

$$\frac{\partial \log f_1}{\partial n_2} = \log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \tag{27}$$

Equations 7, 8, and 9 give:

$$\frac{\partial \log f_1}{\partial n_1} = -\frac{n_2}{n_1} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_2}{n_1(n_1 + n_2)} \cdot (g_1 - 1) \tag{28}$$

$$\frac{\partial \log f_2}{\partial n_1} = \frac{\partial \log f_1}{\partial n_2} = \log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \tag{29}$$

$$\frac{\partial \log f_2}{\partial n_2} = -\frac{n_1}{n_2} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_1}{n_2(n_1 + n_2)} \cdot (g_1 - 1) \tag{30}$$

The total differential of $\log f_2$ is then:

$$d \log f_2 = \left[\log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2}\right] dn_1 + \left[-\frac{n_1}{n_2} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_1(g_1 - 1)}{n_2(n_1 + n_2)}\right] \cdot dn_2 \tag{31}$$

Assuming that $\log f_2$ is zero when $n_2 = 0$, the integration from $n_2 = 0$ to n_2 at n_1 constant gives:

$$\log f_2 = -\int_0^{n_2} \frac{n_1}{n_2}\cdot\log N_1\cdot\frac{\partial g_1}{\partial n_2}\cdot dn_2 + \int_0^{n_2} \frac{n_1(g_1 - 1)}{n_2(n_1 + n_2)}\cdot dn_2 \tag{32}$$

In the same way we have:

$$d \log f_1 = \left[-\frac{n_2}{n_1}\cdot\log N_1\cdot\frac{\partial g_1}{\partial n_2} + \frac{n_2}{n_1(n_1 + n_2)}\cdot(g_1 - 1) \right] dn_1 + \left[\log N_1\cdot\frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \right] dn_2 \tag{33}$$

Assuming that $\log f_1$ is zero when $n_2 = 0$ and integrating from $n_2 = 0$ to n_2 at n_1 constant we have:

$$\log f_1 = \int_0^{n_2} \log N_1\cdot\frac{\partial g_1}{\partial n_2} dn_2 - \int_0^{n_2} \frac{g_1 - 1}{n_1 + n_2} dn_2 \tag{34}$$

In both 31 and 33 $\frac{\partial g_1}{\partial n_2} dn_2$ may be replaced by dg_1, since n_1 is constant. In practice one takes n_1 equal to the number of moles corresponding to 1000 grams of solvent.

In the case of an electrolyte we may use the Debye-Hückel law for the activity coefficient. We thus have $\frac{\partial \log f_2}{\partial n_2}$ at n_1 constant. Thermodynamics gives then $\frac{\partial \log f_2}{\partial n_1}$, $\frac{\partial \log f_1}{\partial n_1}$, and $\frac{\partial \log f_1}{\partial n_2}$.

Example 2. If $x = 3$, there are two solute species and we need three non-thermodynamic relations. In the case of two dilute electrolytes the Debye-Hückel theory gives:

$$\frac{\partial \log f_2}{\partial n_2}, \quad \frac{\partial \log f_3}{\partial n_3}, \quad \text{and} \quad \frac{\partial \log f_2}{\partial n_3} \quad \text{or} \quad \frac{\partial \log f_3}{\partial n_2}$$

In the case of mixtures of strong electrolytes and weak electrolytes, electrolytes and non-electrolytes, etc., the various formulas of the present paper will depend on the choice of the thermodynamic "description": complete dissociation, incomplete dissociation, no dissociation.

Let us, for instance, consider a solution containing besides the solvent, λ_+ positive ionic species and λ_- negative ionic species obtained by dissolving a certain number of strong electrolytes. We first try to determine the minimum number of neutral components in terms of which the properties of the solution can be studied. Activity coefficients which are thermodynamically significant are average ionic coefficients of neutral components:

$$f_\pm = (f_+^{\nu_+}\cdot f_-^{\nu_-})^{1/\nu} \tag{35}$$

f_+ and f_- are the activity coefficients of the positive and of the negative ions. ν_+, ν_- are the numbers of positive and negative ions in the neutral component ($\nu = \nu_+ + \nu_-$). If z_+ and z_- are the algebraic values of the valences we have:

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{36}$$

The number of neutral components necessary to describe the properties of the solution is at most $\lambda - 1$ (in which $\lambda = \lambda_+ + \lambda_-$) (3) and at least λ_+ or λ_- (λ_+ if $\lambda_+ > \lambda_-$, λ_- if $\lambda_- > \lambda_+$). The neutral components having been chosen, the thermodynamic reasoning developed in this paper applies to the activity coefficients $f_{\pm,i}^{\nu_i}$. For instance, the reciprocity relations 9 become:

$$\frac{\partial \log f_{\pm,i}^{\nu_i}}{\partial n_j} = \frac{\partial \log f_{\pm,j}^{\nu_j}}{\partial n_i} \tag{37}$$

The activity coefficients appearing in 7 and 8 are replaced by $f_{\pm,i}^{\nu_i}$, $f_{\pm,j}^{\nu_j}$, etc.

SUMMARY

It is shown that, at given temperature and pressure, the various activity coefficients of a solution consisting of the solvent and of $x - 1$ solute species satisfy x differential equations of the Gibbs-Duhem type and $\frac{x(x-1)}{2}$ reciprocity relations of the type:

$$\frac{\partial \log f_i}{\partial n_j} = \frac{\partial \log f_j}{\partial n_i}.$$

The knowledge of

$$x^2 - \left[x + \frac{x(x-1)}{2}\right] = \frac{x(x-1)}{2}$$

non-thermodynamic relations between the various $\frac{\partial \log f_i}{\partial n_j}$ and the n_i's is thus required in order to obtain the total differentials of all the $\log f_i$'s, which are then calculated by means of quadratures, supplemented by the assumption that $f_i = 1$ at infinite dilution. After a discussion of certain special forms of the Gibbs-Duhem formulas the correct generalized form of the Duhem-Margules formula is obtained. The introduction of average ionic activity coefficients in the Gibbs-Duhem formula is discussed.

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THE DETERMINATION OF THE DEGREE OF PURITY OF LIQUID SUBSTANCES AND AZEOTROPIC MIXTURES

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Received February 28, 1934

During the last few years (1) the differential ebullioscopic apparatus has been so improved that it now seems possible to propose a standardized type of apparatus and to state the conditions for carrying out the determination of the degree of purity of either single liquid substances or of azeotropic mixtures.

Figure 1 represents the standardized type of ebullioscope for such purposes. This apparatus differs from the former one in that it has two drop-counters, f_1 and f_2, instead of one. To the drop-counter f_2 is sealed a reflux tube by means of which the liquid can be heated with either a small micro-burner, l, or an electric heater. This device enables one to collect a certain quantity of relatively volatile impurities in the upper part of the apparatus and thereby to increase the difference between the boiling point, t_1, measured in the lower part of the ebullioscope, and the temperature of condensation, t_2, measured in the upper part. The two drop-counters enable one to fix the intensity of the heating and to standardize the conditions of the experiment.

The degree of purity of a single liquid substance or of an azeotropic mixture is characterized by the difference $\Delta t = t_1 - t_2$ between the two above-mentioned temperatures. It is evident that, in the case of an absolutely pure single substance or of an ideal azeotropic mixture, this difference Δt is practically zero, because the correction for the difference of pressures at the levels t_1 and t_2, where the temperatures are measured, does not exceed 0.001°C. But since every liquid, even the most highly purified one, contains impurities, certain differences of $\Delta t > 0$ are noted, which depend on the nature and the amounts of the impurities. Since the difference Δt depends upon the degree of dephlegmation of the vapors present in the whole apparatus, the intensity of the heating should remain constant throughout. This condition may be fulfilled by adjusting the rate of flow through the two drop-counters measured by the numbers n_1 and n_2 of drops falling from the latter per unit time for a given intensity of heating; the number of drops depends upon the heat of vaporization and upon the boiling point of the liquid. Our experiments with water have led us to fix for n_1 a value of 40 drops per minute. For other liquids which boil at $t_1 < 100$°C. the following empirical relation can be used:

$$n_1 = \frac{900}{d \cdot L}$$

where L represents the molecular heat of evaporation expressed in kilogram-calories, and d the density of the liquid. When $t_1 > 100$°C. the number of drops should be correspondingly greater. Good results can be obtained with $n_2 = 0.9\,n_1$, or $n_1 = n_2$. The size of the flame of the microburner, l, should be regulated so that this relation can be obeyed.

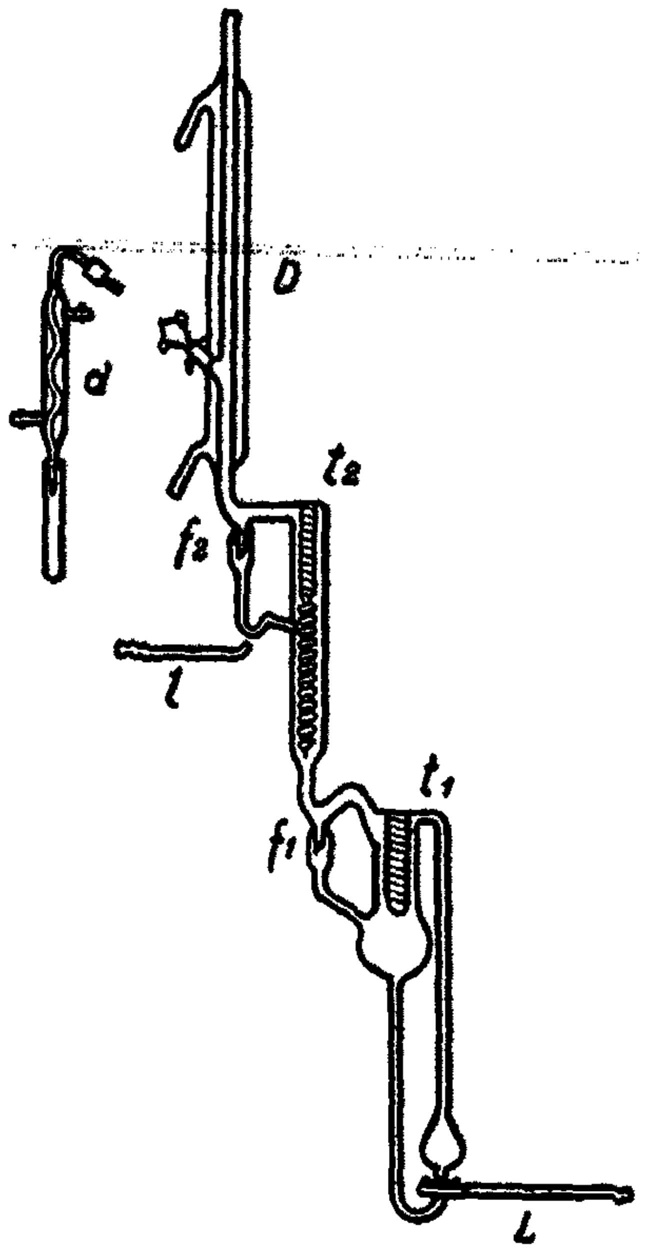

FIG. 1. THE EBULLIOSCOPE

For the estimation of the degree of purity of liquid substances the following measurements should be carried out: (1) the determination of the boiling point and the temperature of condensation of the substance under atmospheric pressure and the comparison of both points with the boiling point of water as the primary standard substance, or of another substance chosen as secondary standard; (2) the determination of the same temperatures after removal by distillation of a small quantity of the liquid.

This last operation seems to be necessary in almost all cases. Indeed, it often happens that very pure liquids contain minute traces of moisture or other impurities which can easily be removed by evaporating several cubic centimeters of the liquid (4). For this purpose the water is removed from the reflux condenser D, the small condenser, d, is joined to the tube provided with a ground joint, and a gradual distillation of 2 cc., 2 cc., and 2 cc. of the liquid is performed. After each distillation the difference Δt is measured. In this way it can be found whether the moisture present in the liquid or introduced as vapor adsorbed by the internal surface of the ebullioscope can be removed by this simple operation.

The investigation should be carried out as follows: (1) Before use the walls of the apparatus should be thermally isolated. Tube 1 should be wrapped with wet asbestos strips; after they are dry they fit closely to the surface of the Pyrex glass. The tubes in which the temperatures are measured are also wound with strips which are fastened round the tubes by means of thin copper wire. On top of the burner L an asbestos roof of conical shape is provided. (2) The ebullioscopic apparatus should be carefully dried and filled with a given amount of liquid under investigation (15 cc.). After allowing the liquid to boil for ten to fifteen minutes the apparatus is emptied, then refilled with a new portion of the same liquid; the same process is repeated, the liquid being once more poured out. Finally the apparatus is filled with 50 cc. of the liquid to be actually measured. (3) The temperatures should be determined with the accuracy of ±0.001°C. For this purpose the electrical resistance thermometer or the Beckmann mercury thermometer (modified by me) or that of Roberteau, etc., may be used. When Roberteau's thermometer is selected, the enlargement between the scale and the bulb called "grain" must be immersed in mercury. Each thermometer should be immersed to the same extent in both tubes, t_1 and t_2. (4) The intensity of the heating with both burners should be regulated as already stated. (5) The determination of the two above-mentioned temperatures should be carried out by using the same thermometer. For this purpose the method of successive measurements should be applied (an example of this method is given in table 1). The boiling point of water or other substance chosen as the standard liquid (2, 5) is measured simultaneously. If another substance than water is used as standard, its boiling point should differ only slightly from the boiling point of the liquid under examination, so that its boiling point may be measured by transferring the same thermometer from one ebullioscope to another. (6) After having determined the difference Δt (first difference) the small condenser d is joined to the side-tube of the condenser D and the water is removed from this condenser. Afterwards three 2-cc. portions of the liquid are carried over into the small test tube by successive distillation. After each distillation the determination of the difference Δt is carried out. If all the successive differences, Δt, Δt_1, Δt_2, Δt_3, or at least the last two remain practically constant, $\Delta t > \Delta t_1 = \Delta t_2 = \Delta t_3$ or $\Delta t > \Delta t_1 > \Delta t_2 = \Delta t_3$, the value Δt_2 may be accepted as a basis for characterizing the degree of purity of the investigated liquid. If, however, the above-mentioned differences gradually decrease, $\Delta t > \Delta t_1 > \Delta t_2 > \Delta t_3$, it proves that the impurity cannot be removed by this operation and that consequently the second difference, Δt_1 ought to be accepted as the characteristic value for the degree of purity of the sample investigated. In both cases all the successive differences, Δt, Δt_1, Δt_2, Δt_3, should be stated in order to give some idea as to the nature of the impurities present in the liquid under examination. For the present it appears that actually the following scale may be accepted for characterizing the degree of purity of liquid substances:

TABLE 1

Determination of the purity of isopropyl alcohol

TIME	t_1	t_2[*]	Δt	t_{Bar}	ΔT
11.00	4.978			2.430	
11.02	4.979			2.430	
11.04	4.979			2.429	
				2.430	
				2.430	
11.10	(4.979)	4.783	0.196	2.430	
11.12	(4.979)	4.786	0.193	2.430	
11.14	(4.979)	4.780	0.199	2.430	
First difference			0.196		
11.18	4.979				
11.20	4.979				
11.22	4.979				
11.28	(4.979)			3.013	1.966
11.30	(4.979)			3.013	1.966
11.34	(4.979)			3.013	1.966
11.36					
11.38					
11.40	4.979				
11.42	4.979				
11.44	4.979				

[*] The condensation temperature varies between relatively large limits on account of the presence of a large amount of volatile impurities.

Degree of purity	*Limits in degrees for the difference Δt*
First degree of purity (I)	1.00 to 0.10
Second degree of purity (II)	0.10 to 0.05
Third degree of purity (III)	0.05 to 0.02
Fourth degree of purity (IV)	0.020 to 0.005
Fifth degree of purity (V)	0.005 to 0.000

If the liquid is, however, characterized by the fifth degree of purity, a more careful investigation ought to be carried out with the help of a more sensitive differential ebullioscope.

At the present time the differential ebullioscope with several sections (3) seems to be the most convenient for this purpose.

The degree of purity of isopropyl alcohol (Schering-Kahlbaum) was determined by means of a standardized ebullioscope (table 1). Benzene, selected as a secondary standard, has a boiling point $t_{\mathrm{Bar}} = 80.122$°C. at 1 atmosphere. The first difference, Δt, between the boiling point and the condensation temperature was determined. The difference between the boiling points of the two liquids examined is equal to $\Delta t = 1.966$. After the introduction of the correction for the true value of the degree, the difference, $t_{\mathrm{Bar}} - t_1 = \Delta T$, becomes equal to 2.060, therefore the boiling point of isopropyl alcohol, t_a, equals 82.18°C. By successive distillation of three 2-cc. portions of the liquid, the following results have been obtained:

$\Delta t_1 = 0.195$ $\quad \Delta T_1 = 2.098$ $\quad t_a' = 82.22$
$\Delta t_2 = 0.144$ $\quad \Delta T_2 = 2.108$ $\quad t_a'' = 82.23$
$\Delta t_3 = 0.083$ $\quad \Delta T_3 = 2.124$ $\quad t_a''' = 82.25$

CONCLUSIONS

Control of the purity for the given sample of isopropyl alcohol proves that the impurities cannot be removed by distillation of a small quantity of the liquid. In accordance with the scale proposed above, the degree of purity seems characterized by the first difference, $\Delta t = 0.195$. The boiling point of the liquid, t_a, is equal to 82.22°C. at 1 atmosphere, which is 2.10° higher than the boiling point at 1 atmosphere of benzene, the secondary standard substance. After distillation by help of a rectification column with twenty-one bulbs the determination of the degree of purity of the purified isopropyl alcohol has been carried out. The following result has been obtained: $\Delta t = 0.010$; $\Delta t_1 = 0.009$; $\Delta t_2 = 0.009$; $\Delta t_3 = 0.008$; $\Delta T_3 = 2.17$; $t_a''' = 82.29$° ($p = 1$ atmosphere).

It follows that in accordance with our scale, the sample of the purified isopropyl alcohol can be considered as having the IV-th degree of purity, Δt being equal to 0.009°, and the boiling point to 82.29°. The boiling point of the investigated isopropyl alcohol is 2.17° higher than the boiling point of benzene, the secondary standard substance ($p = 1$ atmosphere).

SUMMARY

The application of a standardized differential ebullioscope for determining the degree of purity of single liquid substances and azeotropic mixtures has been described. Brief instructions are given for executing the investigation. A scale for characterizing the relative degree of purity of liquid substances and azeotropic mixtures has been proposed.

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X-RAY STUDIES ON THE HYDROUS OXIDES. VI

ALUMINA HYDRATES

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Received May 8, 1934

Two years ago (19) it was concluded, as a result of x-ray and dehydration studies, that only two hydrates of alumina exist: γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite) and α-$Al_2O_3 \cdot H_2O$ (diaspore). No indication was found for the existence of a second trihydrate, α-$Al_2O_3 \cdot 3H_2O$ (Fricke's bayerite), or of a second monohydrate, γ-$Al_2O_3 \cdot H_2O$ (böhmite). From the available evidence, it was believed that precipitated alumina was hydrous "δ-Al_2O_3" rather than hydrous γ-$Al_2O_3 \cdot H_2O$. In the light of recent developments it now appears that certain of these conclusions must be modified and extended.

α-ALUMINA TRIHYDRATE

While our first paper was in the process of publication, an article by Fricke and Severin (7) appeared in which definite evidence was presented to prove that α-$Al_2O_3 \cdot 3H_2O$ (bayerite), isomeric with gibbsite, exists. The α-$Al_2O_3 \cdot 3H_2O$ gives a distinctive x-ray diffraction pattern and a dehydration isobar characteristic of a trihydrate. Synthetic γ-$Al_2O_3 \cdot 3H_2O$ is formed by the slow hydrolysis of aluminates (Bonsdorff and Goudriaan). On the other hand, if the separation takes place relatively quickly, the metastable isomer, α-$Al_2O_3 \cdot 3H_2O$, is first formed and goes over spontaneously into γ-$Al_2O_3 \cdot 3H_2O$ in the course of a few weeks in contact with dilute alkali. We failed to observe the formation of α-$Al_2O_3 \cdot 3H_2O$ either by the method of Goudriaan or that of Bonsdorff, since the precipitate remained in contact with the alkali for 30 days before it was subjected to x-ray analysis and was therefore largely γ-$Al_2O_3 \cdot 3H_2O$.

A pure sample of α-$Al_2O_3 \cdot 3H_2O$ sent us by R. P. Rooksby has been examined by the x-ray diffraction method. Comparison of the x-ray diagram of α-$Al_2O_3 \cdot 3H_2O$ shows that some of our samples, previously considered to be mixtures of γ-$Al_2O_3 \cdot 3H_2O$ and δ-Al_2O_3, contained considerable amounts of α-$Al_2O_3 \cdot 3H_2O$. For example, diagrams 3, 4, and 6 of figure 3 and 1 to 5 and 8 of figure 6 (20) are for samples that we now know to be largely α-$Al_2O_3 \cdot 3H_2O$.

γ-$Al_2O_3 \cdot H_2O$ VERSUS "δ-Al_2O_3"

More than twelve years ago L. H. Milligan (16) dehydrated a sample of artificial gibbsite in a current of air containing a known amount of water vapor. The dehydration isobar showed conclusively that the sample was a trihydrate, but it gave no indication whatsoever of the formation of a monohydrate. Since both Rooksby (17) and ourselves have obtained a material that gives the same x-ray diffraction pattern as γ-$Al_2O_3 \cdot H_2O$ (böhmite) by the thermal dehydration of α-$Al_2O_3 \cdot 3H_2O$ (gibbsite), it is important to explain, if possible, why the isobars fail to reveal the presence of a monohydrate.

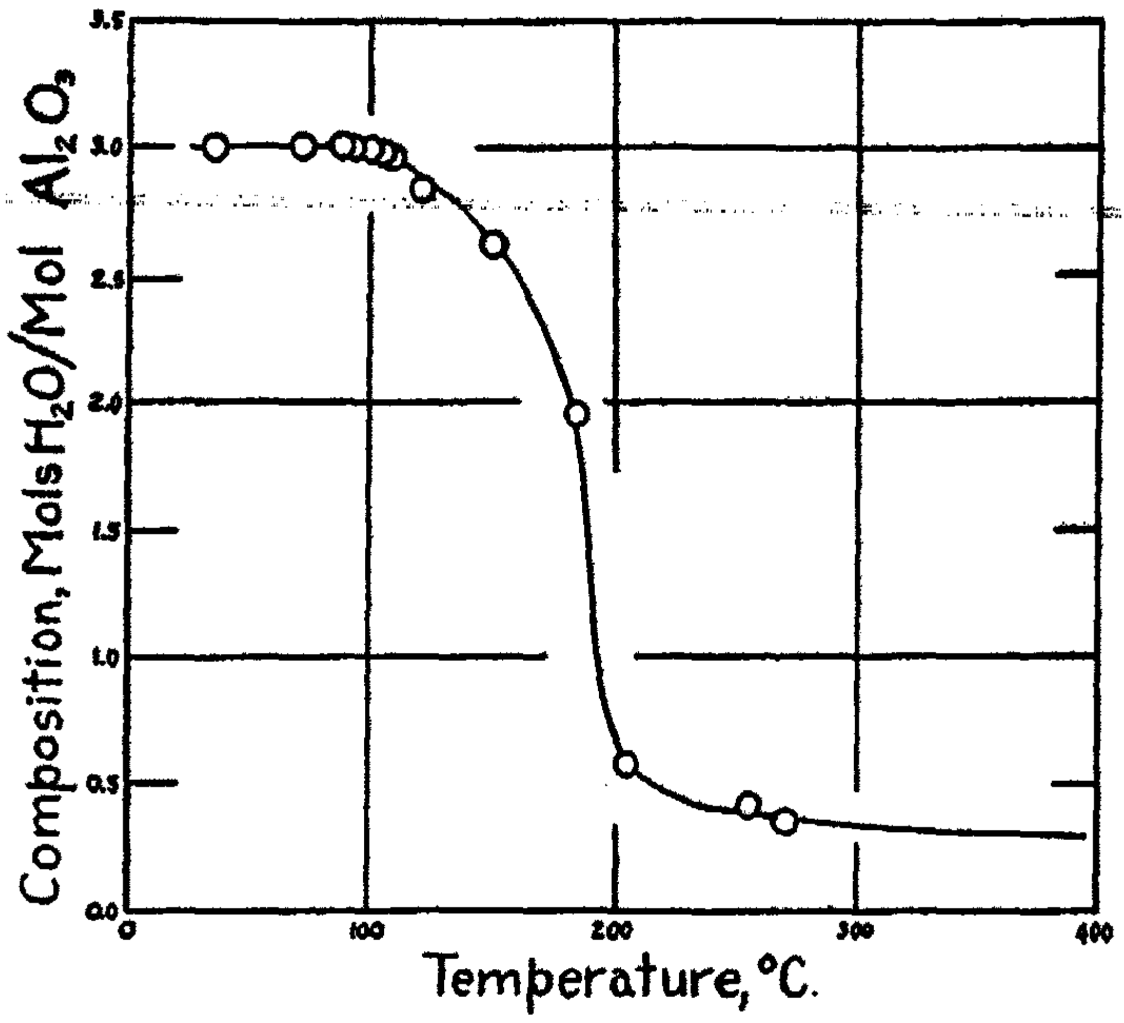


FIG. 1. DEHYDRATION ISOBAR OF γ-$Al_2O_3 \cdot 3H_2O$ (SYNTHETIC GIBBSITE)

Dehydration isobar of artificial gibbsite

A sample of γ-$Al_2O_3 \cdot 3H_2O$ was dehydrated in an apparatus similar to that of L. H. Milligan previously described (20). Special care was taken to secure equilibrium values. It was found that many days were required at the lower temperatures and many hours at the higher temperatures. The results are shown graphically in figure 1. It is apparent that the isobar gives no evidence whatsoever of the formation of monohydrate. X-ray analyses of samples taken at intervals from a second container give the results shown in table 1.

A dehydration isobar almost identical with figure 1 was obtained with gibbsite by Fricke and Severin (7). They also made the isobars for the α-trihydrate or bayerite and for both α-$Al_2O_3 \cdot H_2O$ (diaspore) and γ-$Al_2O_3 \cdot H_2O$ (böhmite). These curves, reproduced in figure 2, are noteworthy since extreme care was taken to ensure equilibrium. In some cases several weeks were required to get a single point, and the value recorded was taken only after the system remained in equilibrium for from eight to twenty-five days.

TABLE 1

X-ray diffraction data obtained during the dehydration of artificial gibbsite

TEMPERATURE	TYPE OF PATTERN
degrees C.	
35–150	γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite)
185	γ-$Al_2O_3 \cdot H_2O$ (böhmite) and γ-$Al_2O_3 \cdot 3H_2O$
205–410	γ-$Al_2O_3 \cdot H_2O$

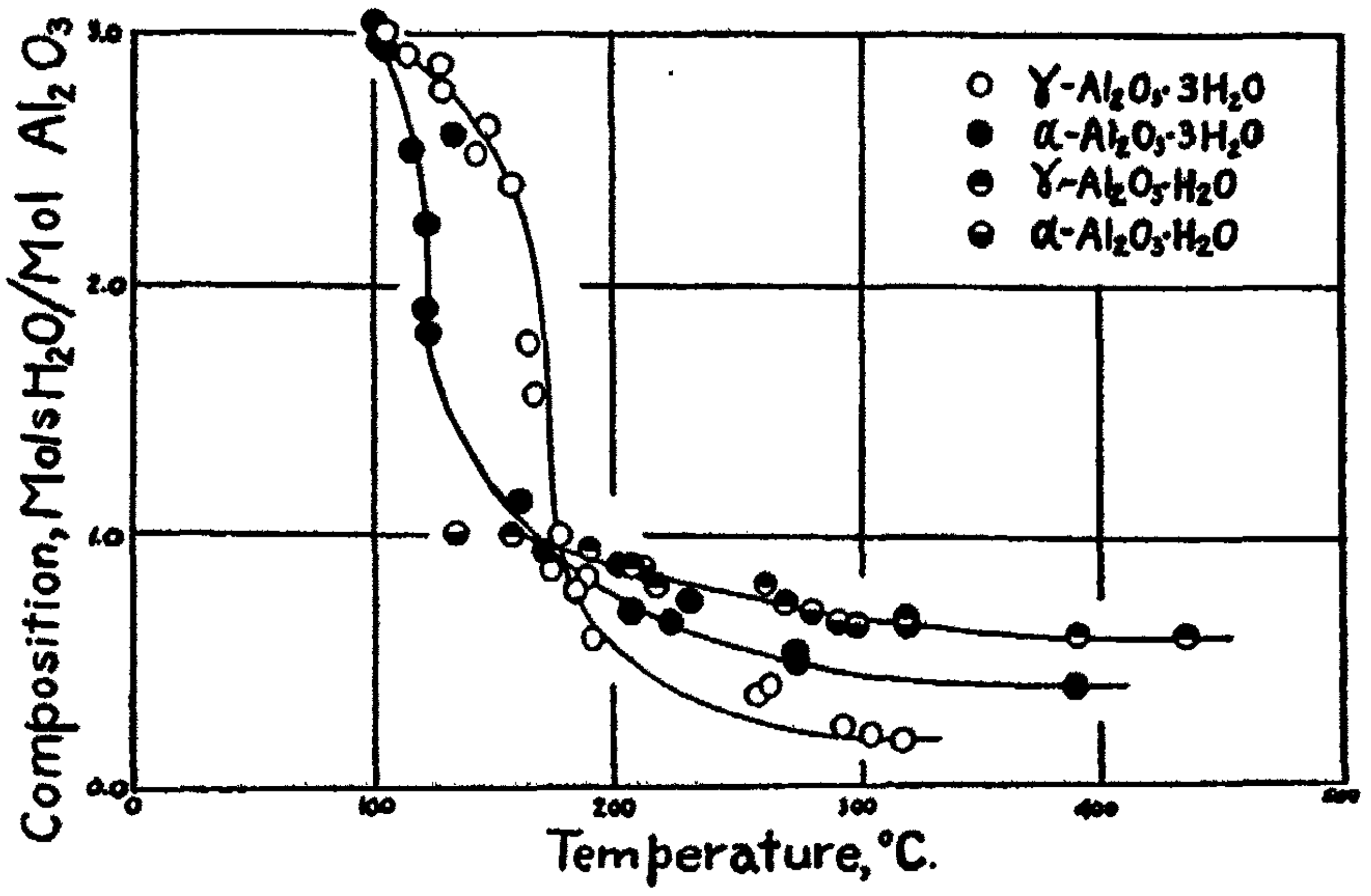


FIG. 2. DEHYDRATION ISOBAR OF α- AND γ-$Al_2O_3 \cdot 3H_2O$ AND α- AND γ-$Al_2O_3 \cdot H_2O$

After Fricke and Severin

In the light of the above work there can be no question about the facts. The monohydrate formed by the decomposition of γ-$Al_2O_3 \cdot 3H_2O$ does not undergo decomposition at a definite temperature as a real hydrate usually does. Indeed in the experiment shown in figure 1, a sample at 410°C., having a composition of approximately $Al_2O_3 \cdot 0.34H_2O$, gave the x-radiogram of γ-$Al_2O_3 \cdot H_2O$ only. This would be impossible if the hydrate were behaving in a normal way. Furthermore, Fricke and Severin's curve for the monohydrate is a typical desorption curve showing no indication whatsoever of a break. It is this sort of evidence which formerly led us to conclude that the alleged monohydrate was not a true hydrate but an alumina with adsorbed water.

The only evidence advanced by Rooksby (17) in support of the view that the initial product of the thermal dehydration of γ-$Al_2O_3 \cdot 3H_2O$ is a monohydrate, was an analysis of the product. But the dehydration curves of L. H. Milligan, Fricke and Severin, and ourselves show that this composition was accidental and could not possibly have been an equilibrium value. More recently Edwards and Tosterud (6) claimed that the compound formed by heating precipitated alumina under pressure, analyzed for a monohydrate, gave the γ-$Al_2O_3 \cdot H_2O$ x-ray pattern, and exhibited a thermal arrest in the heating curve. The first two lines of evidence will not definitely distinguish between a monohydrate and a hydrous alumina with the right amount of adsorbed water, and an arrest in the heating curve of an oxide–water system does not necessarily indicate the presence of a true hydrate (10). In this case the arrest might be offered as evidence of a polymorphic change from "δ-Al_2O_3" to γ-Al_2O_3. However, preparations which give the γ-$Al_2O_3 \cdot H_2O$ (böhmite) pattern can be obtained in well-defined macroscopic crystals which analyze for monohydrate. Thus Fricke and Severin (7) obtained it by heating commercial alumina trihydrate to 350–370°C. at a pressure of 200 atmospheres. Hüttig and Peter (11) prepared a similar product by heating the trihydrate in a bomb tube at 200 atmospheres. Particularly good crystals were formed by heating 4–20 per cent aluminum nitrate containing up to 20 per cent of nitric acid at 320–360°C. and 200 to 300 atmospheres (12, 13). In the light of this positive evidence there can no longer be any doubt that böhmite is γ-$Al_2O_3 \cdot H_2O$. But having reached this conclusion one is obliged to explain the absence of any sign of a break corresponding to the monohydrate in the dehydration isobars of γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3 \cdot H_2O$.

Interpretation of the dehydration isobars

Application of the phase rule to the two-component system hydrate–oxide–water vapor, shows that the system should be univariant. The type of isobar is given by the dotted lines in figure 3. Theoretically, the curve should drop to zero composition at a definite temperature, but actually the isobars are usually rounded off, as shown in the figure by the broken line *ADC*. This is due to a loss of part of the water below the true decomposition temperature of the mass of the hydrate on account of lattice distortion, strain in the crystals, and variation in crystal size. Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line *AE* in figure 3. It is precisely this last type of curve which Fricke and Severin obtained for both α- and γ-$Al_2O_3 \cdot H_2O$.

We can now explain the persistence of the x-radiogram of the monohydrate where it would ordinarily not be expected to exist. The x-radiogram for the monohydrate should persist along the broken curve *ADC*, because some monohydrate exists as such, and the very highly hygroscopic γ-Al_2O_3 (1, 2, 4, 5, 15, 18, 21), formed by partial decomposition of the former, is either amorphous or too finely crystalline to be detected by x-ray analysis.

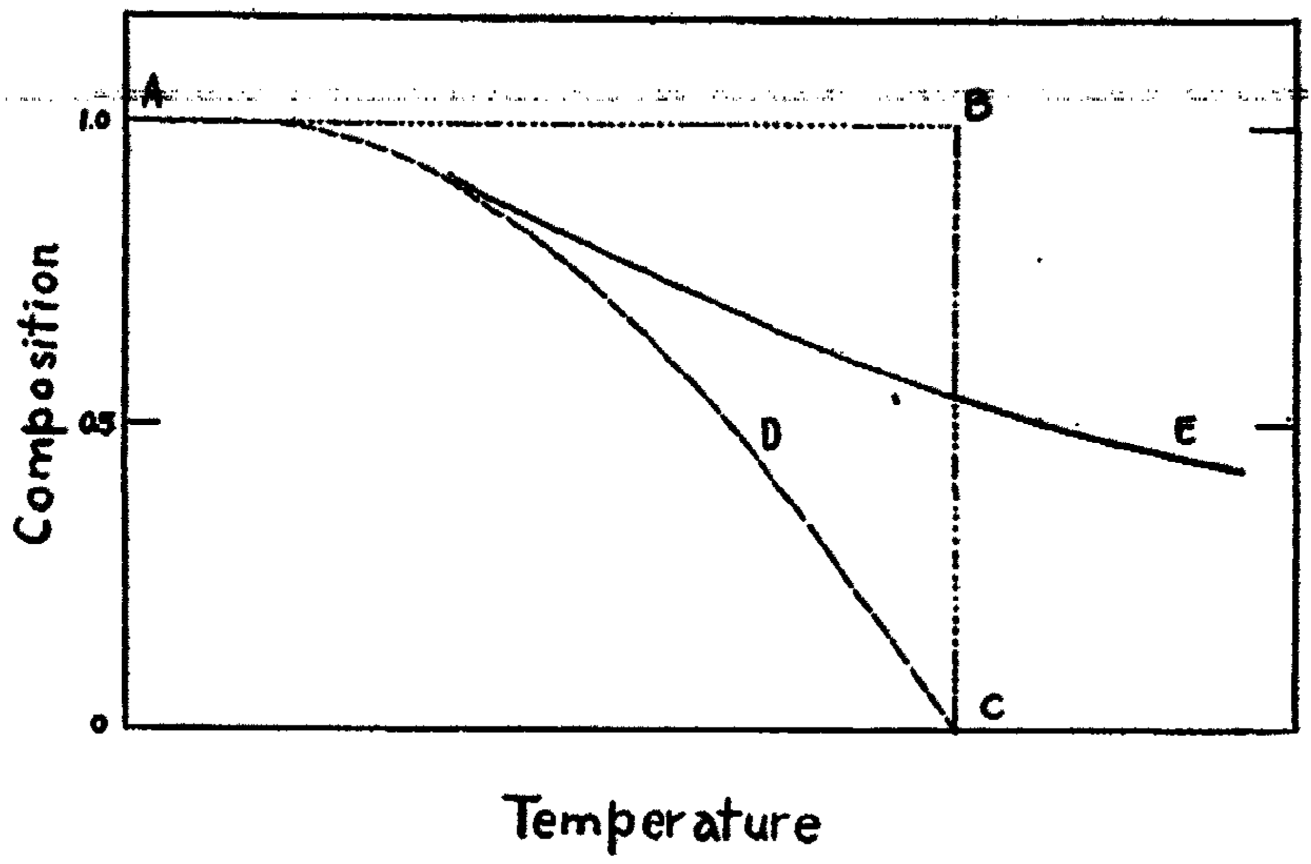


FIG. 3. ISOBARIC EQUILIBRIUM IN THE SYSTEM HYDRATE–OXIDE–WATER VAPOR

In the case of a higher hydrate decomposing first into a lower hydrate and finally into the anhydrous substance, it is apparent that under the conditions noted above, the isobar will fail completely to detect the lower hydrate. In figure 4 the theoretical curves for the case of a trihydrate decomposing to a monohydrate and this in turn to the oxide are given by the dotted lines. The actual experimental curve is given by the solid line. The composition of the trihydrate remains constant until at point *F* some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along *FK* and along *KH* all the trihydrate decomposes rapidly, giving monohydrate. Now at this temperature the lower hydrate loses water to point *O* and hence the line *FKH* continues past the theoretical composition of the monohydrate to the point *O*. This decomposition of the monohydrate gives the highly adsorptive γ-oxide, the presence of which causes the dehydration to proceed along the line *HOE* for the reason given above.

Although the case under consideration is unusual it is not unique. Thus a curve somewhat similar to the one shown in figure 4 is obtained for the dehydration of gypsum, which yields plaster of Paris as an intermediate product (3, 4, 8, 9, 14). The latter compound is said to be $CaSO_4\cdot 0.5H_2O$, but this would not follow from the dehydration curve, which is like *KHE* in figure 4 rather than like *GHB*. Here again, the highly hygroscopic character of the anhydrite resulting from the decomposition of hemihydrate adsorbs a part of the water, and the dehydration of this hydrous material determines the form of the curve.

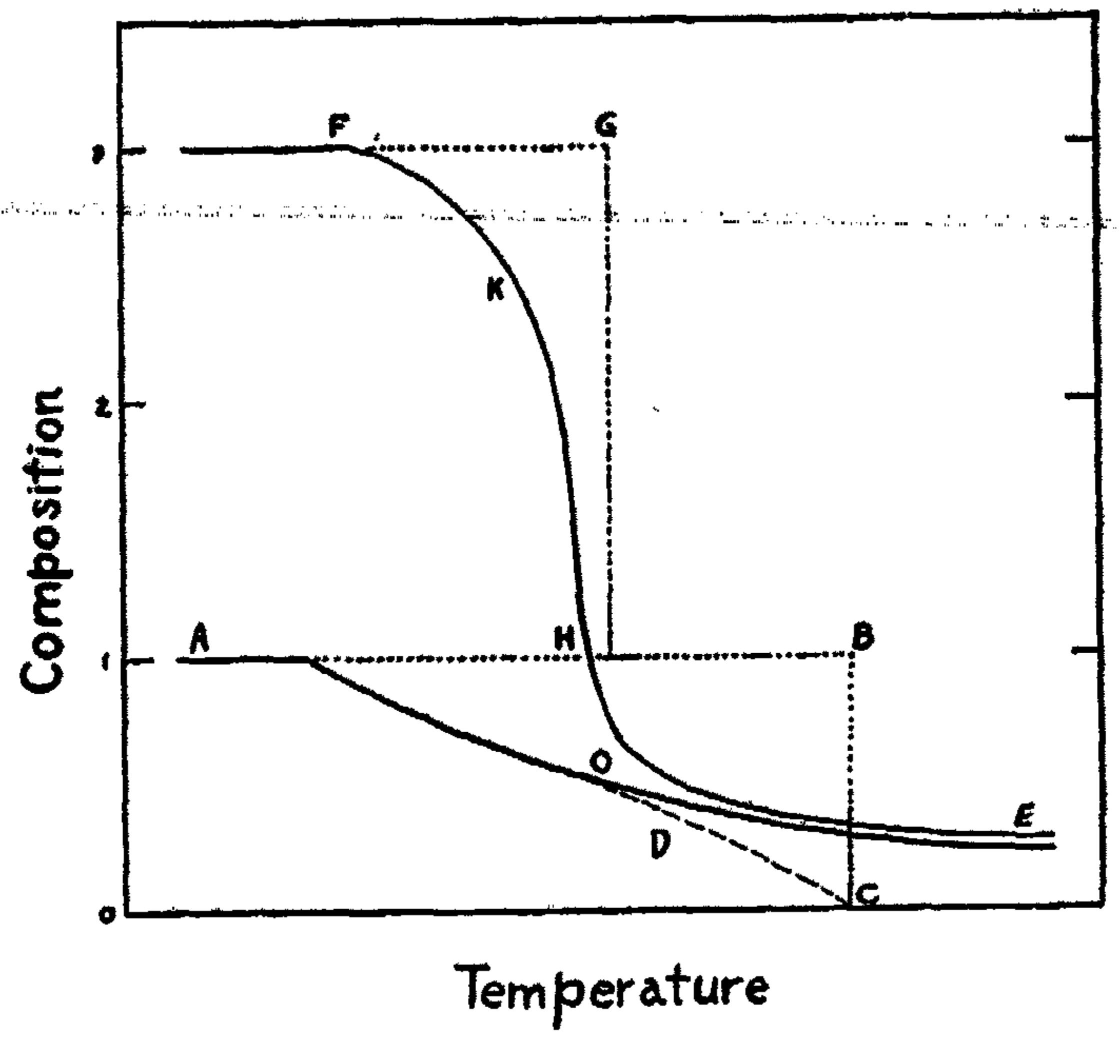


FIG. 4. ISOBARIC EQUILIBRIUM IN THE SYSTEM HYDRATE–LOWER HYDRATE–WATER VAPOR

SUMMARY

The following is a brief summary of the results of this investigation:

1. Slow hydrolysis of an aluminate solution gives a definite metastable alumina hydrate, α-$Al_2O_3\cdot 3H_2O$ (bayerite), different from γ-$Al_2O_3\cdot 3H_2O$ (gibbsite). Aging of this metastable hydrate, especially in contact with alkali, gives γ-$Al_2O_3\cdot 3H_2O$. The present authors overlooked the labile modification since they allowed the products made by the method of Goud-

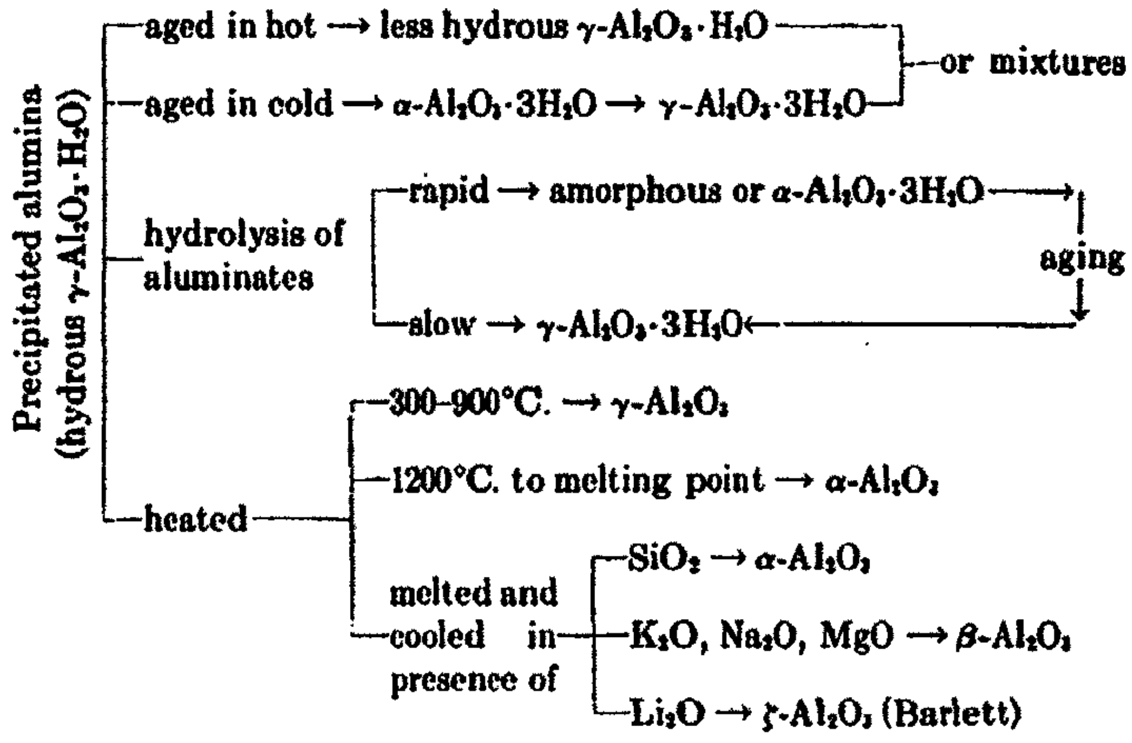
riaan and Bonsdorff to stand in contact with alkali for 30 days. That α-$Al_2O_3 \cdot 3H_2O$ is a definite hydrate has been conclusively proven by dehydration isobars obtained recently by Fricke and Severin.

2. Dehydration isobars of γ-$Al_2O_3 \cdot 3H_2O$ made by L. H. Milligan over twelve years ago, and by Fricke and Severin, and by the present authors more recently, show no indication whatsoever of the formation of a monohydrate. However x-ray examination of the intermediate dehydration product gives the pattern attributed to γ-$Al_2O_3 \cdot H_2O$ (böhmite). This is the same material that the present authors formerly considered to be hydrous "δ-Al_2O_3" because of the form of the dehydration curve.

3. Well-defined macroscopic crystals of γ-$Al_2O_3 \cdot H_2O$ have been made (Fricke and Severin, Hüttig and Peters, Ipatiew), but the dehydration isobar of the compound is a typical desorption curve.

4. In this paper an explanation is suggested for the apparently anomalous behavior of the dehydration isobars of both γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3 \cdot H_2O$, based on the fact that the thermal decomposition of the latter gives a very highly adsorptive oxide (γ-Al_2O_3) which adsorbs most of the water vapor. Dehydration of this hydrous oxide gives a bivariant curve.

5. The various transformations of precipitated alumina may be tabulated in the following diagram, which is a revision of the diagram given in Part I of this series of papers:



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THE CONSTANCY OF THE URANIUM-ACTINIUM RATIO IN MINERALS[1]

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Received May 18, 1934

The status of the actinium series has always been a subject of conflicting experimental findings and of interpretations leading to controversies. Boltwood (1), in 1908, showed that the actinium series was associated with uranium and not with thorium. The determination of the fraction of the uranium atoms disintegrating to form the actinium series, earlier called the "branching ratio" and later called the "activity ratio," has been accomplished by three distinct methods: First, by the determination of the relation between the alpha activity of thin films of protoactinium and pure uranium oxide; second, by the determination of the relation between the alpha activity of thin films of actinium and uranium oxide; third, by the determination of the relation by the comparison of the active deposits from actinon.

Numerical ratios from the first two methods are abundant in the literature: Boltwood (1), 1908, 4 per cent; Fussler (2), 1917, 2.2 to 3.3 per cent; Hahn and Meitner (4), 1919, 3 per cent; Meyer (5), 1920, 4 per cent; Widdowson and Russell (8), 1923, 2.9 per cent; Piccard and Kessler (7), 1924, 5 per cent; Wildish (9), 1930, 1.5 to 5.16 per cent; Gleditsch and Foyn (3), 1932, 2.7 per cent; A. von Grosse (11), 1932, 4 per cent. Meyer and Hess (6) were the only ones to use the active deposit of actinon to show the ratio constant.

A. von Grosse in determining the ratio as a constant, 4 per cent, used five minerals, one of which was the carnotite used by Wildish to find his 5.16 per cent ratio. von Grosse claims that zirconium is a better reagent than tantalum for the adsorption of protoactinium, which Wildish and others regard as the nearest analogue of protoactinium. Having on hand two minerals used by von Grosse and four of those used by Wildish, we undertook to determine the constancy of the ratio by a method independent of the chemistry of protoactinium, namely the method of Meyer and Hess (6). This method, however, does not give the percentage ratio, but does supply evidence as to the constancy of the ratio.

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[1] This paper was read at the Midwestern Regional Meeting of the American Chemical Society held at Kansas City, Missouri, May 4, 1934.

METHOD

The method of Meyer and Hess (6), for the determination of the relative amounts of actinium in ore solutions by means of the active deposit of actinon, was modified for our experiments. Their method consisted of passing air through a solution of the mineral contained in a liter flask and into a rectangular brass box, which contained an insulated brass plate, 2 × 12 cm. The brass plate was 1 cm. from the bottom of the brass box, the inner dimensions of which were 4 × 15 × 3 cm., and was charged negatively to a potential of 460 volts. The air was allowed to flow through the apparatus at a known rate for 1 hour. The activity of the plate was determined by measuring it in a condenser connected to a Wulf string electrometer. The success of the method depends upon the maintenance of a reproducible rate and time of air flow through the apparatus.

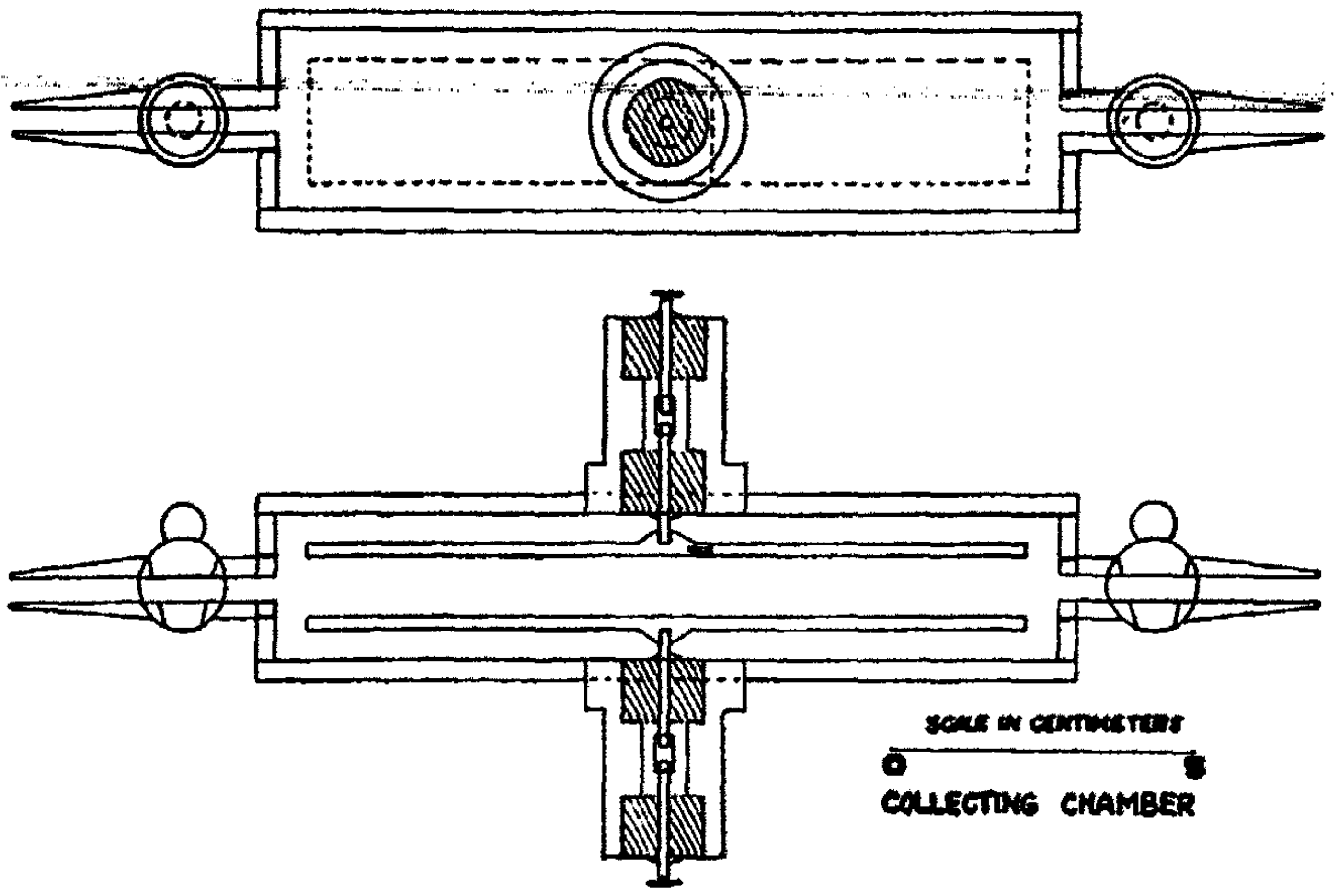

Fig. 1. Collecting Chamber

For our experiments the method was modified so that, using the same flow of air and the same potential on the collecting plates, the apparatus allowed the simultaneous deposition of the active deposit from the actinon continually produced in the solution of two different minerals, thereby eliminating effects due to fluctuations in the rate of flow of the air. The collecting chambers differed from those used by Hess and Meyer; two insulated brass plates were placed 1 cm. apart in a rectangular brass box with inner dimensions 3 × 13 × 2 cm. (figure 1). The upper plate of each chamber was maintained at a negative potential of 500 volts; the lower plate was connected through the ground to the positive side of the source. The upper plate was removable. Two similar, Drechsel type, gas-washing cylinders, of 600-cc. capacity and equipped with spray bubblers, held the solutions under test.

A stream of air is forced through an air meter, through the first solution, through a glass wool plug and drying tube, and thence into the first collecting chamber. From this chamber, the air passes into a 7-liter carboy, where the actinon remaining in the air decays completely, and thence through the second solution and collecting chamber. This air stream removes the actinon from the solution of the ore, where it is being formed continually, and carries it into the chamber in which the actinon decays to produce actinium A. This immediately decays to produce positive ions of actinium B, which are deposited in the electric field on the negatively charged upper plate.

Before a run was started, the air was allowed to pass through the solutions and around the chambers through an alternate path; this procedure removed any radon that might have accumulated in the solutions. The air was then shunted into the chambers by manipulating the stopcocks, and the upper plates charged by a small generator. The runs were all of one hour duration, for which time the air flow was between 120 to 180 liters.

The upper plates were then removed and their activities determined alternatively in a Wulf (10) bifilar, quartz fiber electroscope. In order for the plates to be placed inside of the ionization chamber of the electroscope, they were constructed in two sections, mortised together (figure 1). This joint was broken and each section set in place in a specially constructed glass rack, which fitted rigidly into the ionization chamber of the electroscope. Four values of the activity of each plate were determined for accurate time intervals after the conclusion of the deposition.

Although the time taken in reading the electroscopic drift was from 0.5 to 5 minutes, the decay of actinium B is so rapid that only the average activity is gotten for that time interval. In order to obtain the instantaneous activity for the time at which reading is begun, the following formula must be applied: $A = \bar{A}t/(1 - e^{-\lambda t})$, where A is the instantaneous activity, $\bar{A}$ is the average activity which is obtained from reading the electroscope, t is the time interval of the reading, and λ is the decay constant of actinium B.

After these four values of instantaneous activity for each deposit have been calculated, they are extrapolated back to zero time by means of the formula: $A_0 = Ae^{\lambda t}$, where A_0 is the activity at the conclusion of the deposition, A the instantaneous activity at the time t, t the time elapsed between the conclusion of the deposition and start of the reading of the electroscope, and λ the decay constant of actinium B. These four values for the activity of each deposit were averaged, and the ratio of the actinium in the two solutions under test was obtained. Four such runs were made for each solution of mineral, giving a ratio which was the mean of four means, or which depended upon sixteen individual readings. The ratio of the uranium in the two solutions was obtained from results of gravimetric analysis of the minerals.

Special care was taken to make the volume of air between the solution and the collecting chamber as nearly equal as possible for the two sections of the apparatus. Before the apparatus was used for the determinations, it was tested by determining the activity relation between the halves of a solution prepared by dissolving 200 g. of carnotite ore. The activity of the deposits from these two halves checked closely. Two gas meters were used, one at the source of the air stream and the other at the exit. Checking values were obtained for the amount of air entering and leaving the apparatus.

MATERIALS AND RESULTS

Two carnotites, three pitchblendes, one soddite and one thorianite, four of which were from the same samples used by Wildish (9) and two of which were from the same samples used by A. von Grosse (11), were used for the minerals whose relative actinium–uranium ratios were determined by our experiments.

One method applied to all of these minerals to get them into solution. In each case the mineral was digested in hot concentrated hydrochloric acid–nitric acid for forty-eight hours. The residue was then filtered from the solution, and fused with sodium carbonate containing a small amount of barium chloride. After leaching the fused mass with water, the carbonate residue was filtered off, taken into solution with hydrochloric acid and added to the original solution. If a residue remained after the hydrochloric acid treatment of the carbonate residue, it was again fused, etc. The filtrates from the leach solutions showed an absence of actinon when tested by subjecting them to a run similar to that used with the ore solutions.

Of these seven minerals, only two contained thorium in sufficient quantities to require correction for the activity of thorium B, which was deposited simultaneously with the actinium B. Actinium B decays to a negligible value in 3 hours, while thorium B requires several days. The activity of thorium B can be gotten 5 hours after its deposition, free from the activity of actinium B, and can be extrapolated back to the times of reading the activities of the mixture. In this way the values of the activities of the actinium B can be obtained for the minerals containing thorium. The smallness of the chambers and the high rate of air flow allowed for the activities of actinium B and thorium B to be present in about equal amounts at the time of the readings.

Since solution III, soddite, was used in the first solution cylinder throughout the course of our experiments, and the activities of the other solutions were compared with it, we arbitrarily referred to it as having an actinium-uranium ratio of unity. However, since solution V, G. B. L. pitchblende, was a portion of a sample whose uranium content had been determined very accurately, the ratios were converted so as to refer to it as having an actinium-uranium ratio of unity.

Table 1 summarizes the results of our experiment.

TABLE 1

Actinium-uranium ratio in minerals

Experimental values

MINERALS	SOLUTION NO.	PER CENT OF URANIUM ELEMENT	URANIUM IN SOLUTION	RATIO U/U_{III}	RATIO Ac/Ac_{III}	RATIO Ac/U III AS UNIT RATIO	RATIO Ac/U V AS UNIT RATIO
			grams				
Carnotite[*]	I	30.6	30.6	0.873	0.661	0.753	0.809
Carnotite[†]	II	18.6	18.6	0.532	0.401	0.756	0.811
Soddite[‡]	III	43.8	35.0	1.000	1.000	1.000	1.072
Pitchblende, Bohemian[§]	IV	62.4	27.2	0.777	0.725	0.931	0.998
Pitchblende, G. B. L.[¶]	V	60.6	30.3	0.864	0.804	0.933	1.000
Thorianite[**]	VI	26.7	26.7	0.763	0.688	0.902	0.967
Pitchblende, Wilberforce[‡‡]	VII	53.5	53.5	1.546	1.527	1.012	1.085

[*] Naturita, Colorado; analyzed at the University of Missouri.

[†] Colorado; Wildish, 1930 (ratio of 5.16).

[‡] Belgian Congo; Wildish, 1930.

[§] Bohemia; Wildish, 1930.

[¶] Canada; analyzed at the University of Missouri.

[**] Ceylon; Wildish, 1930.

[‡‡] Canada; G. P. Baxter, 1930, from the same lot used for the Wilberforce lead atomic weight determination.

DISCUSSION AND CONCLUSION

The carnotites, solutions I and II, gave values for the ratio distinctly lower than the other minerals. Carnotite is generally considered a secondary mineral, is not compact, and is susceptible to leaching processes. For these reasons, the carnotites were excluded from the discussion of the constancy of the actinium-uranium ratio.

The individual experimental values for the "ratio Ac/Ac_{III}" are obtained from sixteen readings. These readings had a maximum deviation from their mean not exceeding 5 per cent. Since the uranium was determined gravimetrically, the error would be negligible in comparison with this deviation. Therefore, for our experiments, we place 5 per cent as our probable error. However, for the five minerals other than the carnotites, the maximum deviation from the mean of the "ratio Ac/U" is slightly below 6 per cent. This falls slightly outside of the value set as experimental error.

The results of our experiments seem to justify the conclusion that the ratio of actinium to uranium for the minerals examined is a constant. And since our minerals are representative, we venture to add that the ratio is a constant for all unaltered minerals. However we must add that our method limits us to only a constant ratio and prohibits the assignment of any numerical values to this constant.

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THE KINETICS OF THE OXIDATION OF GASEOUS PROPIONALDEHYDE

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Received April 26, 1934

INTRODUCTION

Aldehydes are of considerable importance in the mechanism of the oxidation of most gaseous organic compounds. As a result a considerable amount of work has been done on the oxidation of gaseous acetaldehyde (1, 3, 4). The acetaldehyde oxidation, however, is complicated and the mechanism is by no means clear. It is therefore of interest to investigate the oxidation of other aliphatic aldehydes where some of these complications might be absent. The present paper deals with the kinetics of the oxidation of gaseous propionaldehyde.

EXPERIMENTAL

The reaction was investigated by introducing propionaldehyde and oxygen separately into a heated vessel and observing the rate of change of pressure as the reaction proceeded. The apparatus was similar to that used in a previous investigation (3). The required temperatures were obtained by means of an electric furnace, the reaction vessel, a 200-cc. Pyrex bulb, being packed into the furnace with coarse iron filings to ensure uniformity of temperature. The temperature was measured with a standardized mercury thermometer, and could be maintained constant to within 1°C.

Propionaldehyde from three sources was used, viz., Kahlbaum, Eastman Kodak, and Eimer and Amend. In each case it was purified by fractional distillation. The three samples gave identical results. Commercial oxygen was obtained from cylinders. It contained 6.4 per cent nitrogen, and was purified merely by drying with phosphorus pentoxide.

EXPERIMENTAL RESULTS

The reaction was investigated from 120°C. to 170°C. No appreciable effect due to the aging of the reaction vessel was noticed after the first ten or fifteen runs. It was also found that neither the degree of evacuation nor the temperature at which this was carried out had any appreciable effect on the succeeding run.

In all runs reported here, oxygen–aldehyde mixtures were made up by introducing the reactants separately into the reaction bulb. (The order of admission had no effect.) This was done because it was found that the maximum pressure decrease associated with the reaction was diminished about 15 per cent, and the rate of reaction was diminished by about 40 per cent, if the reactants were mixed outside the reaction bulb in the presence of a mercury manometer. Tests showed the presence of peroxides under these conditions.

The pressure change accompanying the reaction

As the reaction proceeded the pressure diminished. The maximum decrease amounted to about 73 per cent of the initial partial pressure of the aldehyde. The pressure then slowly rose again. The maximum pressure decreases obtained in a number of typical cases are shown in table 1.

TABLE 1

Maximum pressure decrease

TEMPERATURE	OXYGEN-ALDEHYDE RATIO	INITIAL PARTIAL ALDEHYDE PRESSURE	MAXIMUM PRESSURE DECREASE
degrees C.		*cm.*	*per cent*
150.8	2.52	20.00	73
150.8	1.05	20.00	69
150.8	4.39	12.00	74
150.8	1.36	12.00	71
150.8	1.01	8.85	70
150.8	1.06	9.40	68
150.8	0.90	8.85	63
150.8	0.76	8.75	52
150.8	1.23	5.65	63
139.1	2.86	20.00	75
139.1	3.54	12.00	71
125.3	2.87	20.00	74
125.3	1.96	20.00	76

As shown in table 1, the maximum pressure decrease is constant and independent of the experimental conditions, provided that (a) the partial aldehyde pressure is not much below 8 cm., and (b) the oxygen–aldehyde ratio is not much below 1.00. In as much as the pressure decrease is followed by a pressure increase, it is evident that the reaction proceeds in stages. Since in most cases the maximum decrease is constant, however, there is no doubt that it is justifiable to use the rate of pressure change as a measure of the rate of reaction. In the cases where the full pressure decrease is not reached, it is probably justifiable to employ the same criterion of reaction if we consider only the early part of the process. In consequence we have used the time for the pressure to change from a 15 per cent decrease to a 30 per cent decrease as a measure of the rate of reaction.

The rate of reaction

Complete data for some typical runs are given in table 2, and are plotted in figure 1. It will be seen that as is usual in gaseous oxidation reactions, there is a small induction period.

Table 3 gives values for $T_{30} - T_{15}$ under various conditions.

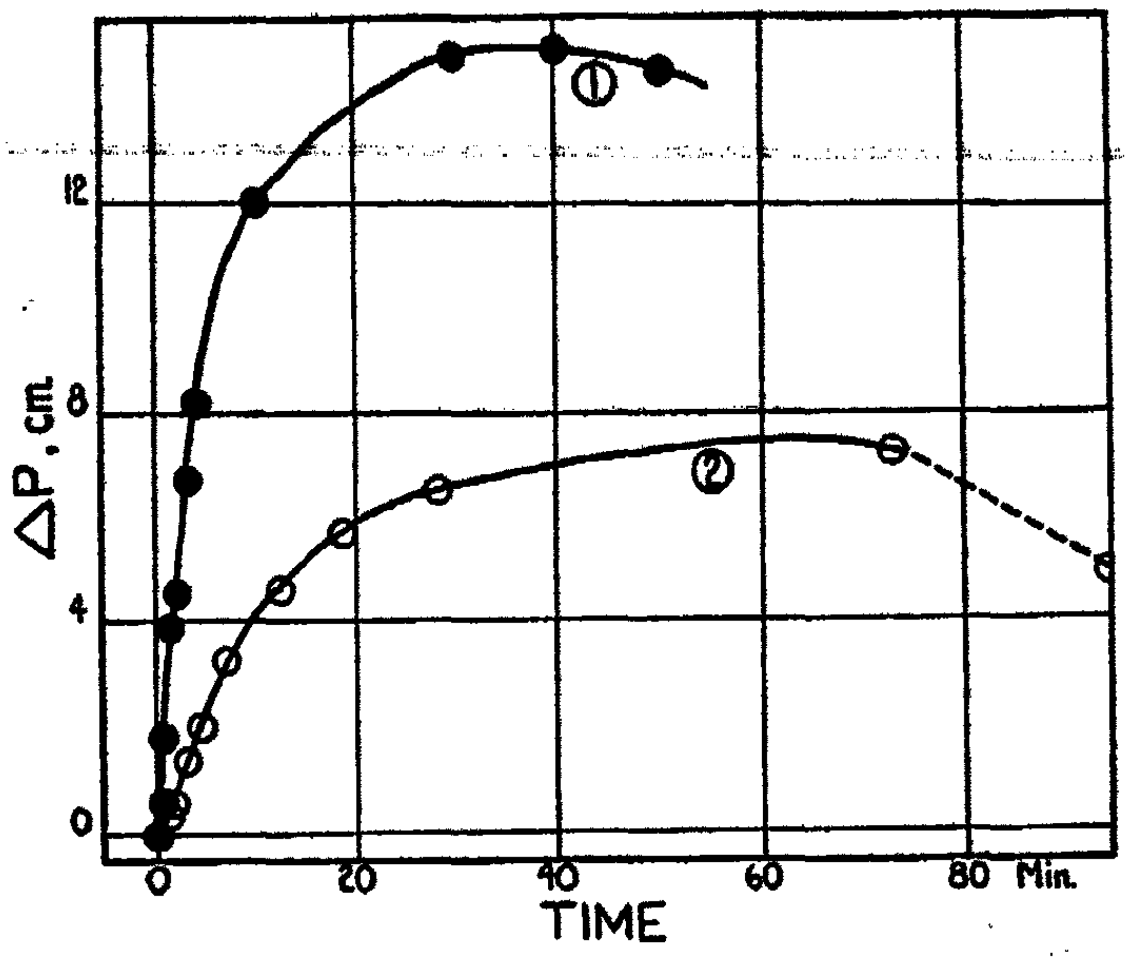

FIG. 1. TYPICAL PRESSURE-TIME CURVES

Temperature, 150.8°C. Curve 1: C_2H_5CHO, 20.0 cm.; O_2, 50.4 cm. Curve 2: C_2H_5CHO, 9.7 cm.; O_2, 38.8 cm.

The effect of pressure

For any given oxygen–aldehyde ratio, the effect of the total pressure on the rate corresponds to an order of about 2.0. The effect of the oxygen concentration on the rate of the reaction is shown by figure 2, in which $T_{30} - T_{15}$ is plotted against the oxygen–aldehyde ratio for various constant initial partial pressures of aldehyde. It will be seen that the rate is virtually independent of the oxygen concentration if the oxygen–aldehyde ratio is above 2.0. When the oxygen concentration is reduced below this value, the rate is somewhat diminished.

TABLE 2

Data for typical runs at 150.8°C.

$P_{ald.}$, 9.70 cm.; O_2/aldehyde, 4.00			$P_{ald.}$, 20.00 cm.; O_2/aldehyde, 2.52		
Time	$-\Delta P$	Per cent ΔP	Time	$-\Delta P$	Per cent ΔP
minutes	*cm.*		*minutes*	*cm.*	
0	0	0	0	0	0
0.5	0.12	1.2	0.5	0.60	3.0
1	0.28	2.9	1	1.80	9.0
1.5	0.45	4.6	1.5	3.85	19.3
3	1.34	13.8	2	4.60	23.0
4.5	2.05	21.1	3	6.65	33.3
7.25	3.24	33.4	4	8.15	40.8
12.5	4.65	48.0	10	12.00	60.0
18.5	5.70	58.8	20	14.50	72.5
28.5	6.50	67.0	30	14.85	74.3
73.5	7.25	74.8	40	14.96	74.8
1680	5.05	52.1	50	14.60	73.0

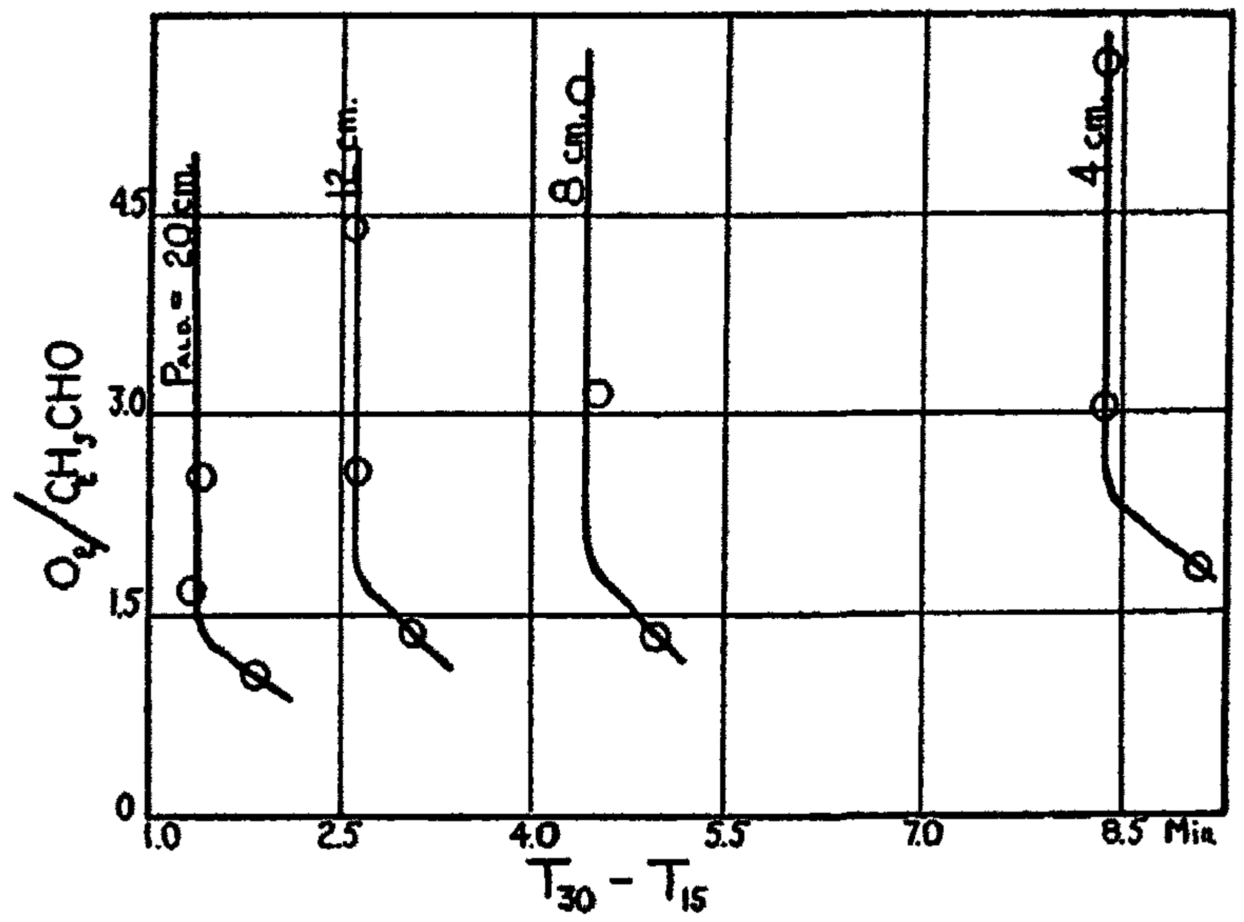

FIG. 2. EFFECT OF OXYGEN CONCENTRATION
Temperature, 150.8°C.

Figure 3 shows the effect of varying the aldehyde concentration while the oxygen concentration is kept constant. The values are given in the form of a log–log plot. From the slopes of the lines the order with respect to aldehyde is found to be between 1.8 and 2.1. Hence, provided the oxygen concentration is not too low, the rate can be approximately expressed by

$$-\frac{d(C_2H_5CHO)}{dt} = K(C_2H_5CHO)^2$$

TABLE 3

Reaction rate data

TEMPERATURE	PARTIAL ALDEHYDE PRESSURE	$\frac{\text{OXYGEN}}{\text{ALDEHYDE}}$	$T_{30} - T_{16}$
degrees C.	*cm.*		*seconds*
150.8	20.00	2.52	85
150.8	20.00	1.68	80
150.8	20.00	1.05	110
150.8	12.00	4.39	155
150.8	12.00	4.37	156
150.8	12.00	2.58	157
150.8	12.00	1.36	184
150.8	8.00	5.46	260
150.8	8.00	5.75	260
150.8	8.00	3.17	270
150.8	8.00	2.10	256
150.8	8.00	1.32	297
150.8	4.00	5.64	502
150.8	4.00	3.02	502
150.8	4.00	1.86	546
167.4	12.00	3.00	76
167.4	8.00	4.00	128
139.1	20.00	2.86	134
139.1	20.00	1.62	144
139.1	20.00	1.62	142
139.1	12.00	3.54	280
139.1	12.00	2.42	282
139.1	8.00	3.20	508
125.3	20.00	1.96	260
125.3	20.00	2.87	266
150.8	8.00	2.58*	320
150.8	20.00	1.17*	111

* Nitrogen added in an amount equal to that of the oxygen.

The temperature coefficient

The temperature coefficient of the reaction has been inferred from three series of runs at constant aldehyde pressures of 20, 12, and 8 cm., using

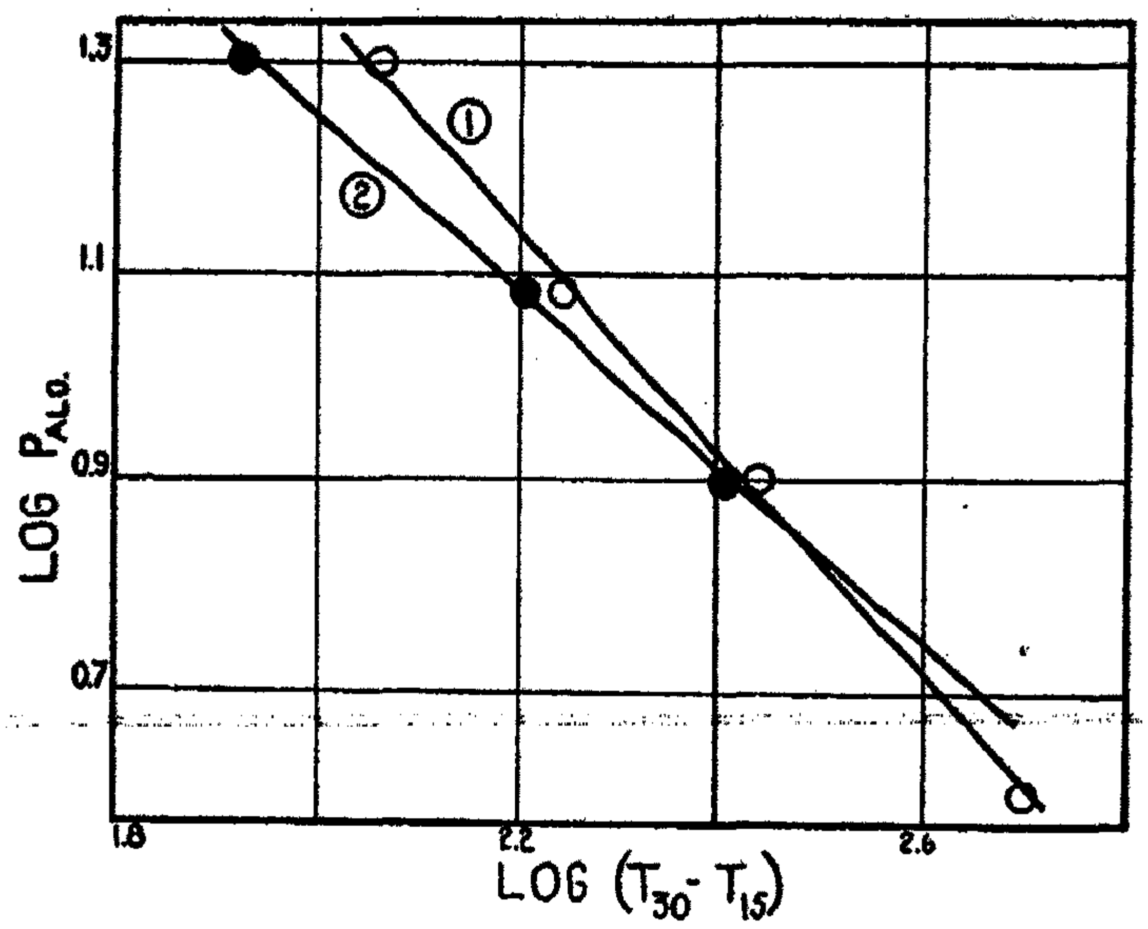

FIG. 3. EFFECT OF PROPIONALDEHYDE CONCENTRATION
Temperature, 150.8°C. Curve 1, P_{O_2} = 20 cm. Curve 2, P_{O_2} = 40 cm.

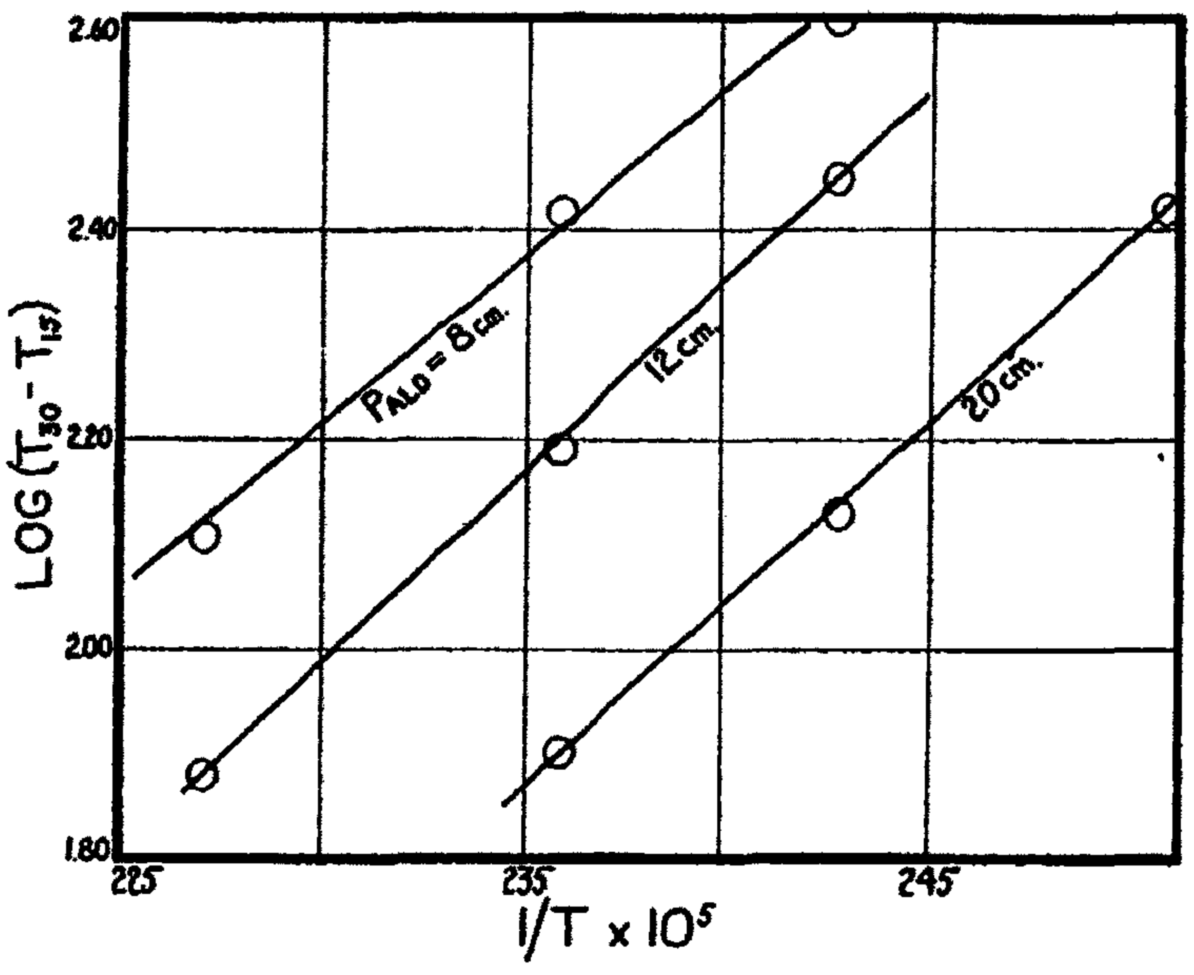

FIG. 4. TEMPERATURE COEFFICIENT

oxygen–aldehyde ratios in the region in which the rate is almost independent of oxygen. The results are shown in figure 4, in which log

$(T_{30} - T_{15})$ is plotted against the reciprocal of the absolute temperature. From the slopes of the lines we obtain the following values for the apparent heat of activation:

P_{aldehyde}	*E in calories per gram-mole*
20 cm.	15,700
12 cm.	16,200
8 cm.	14,400
	Mean = 15,400

The products of the reaction

Some analyses of the gaseous products of the reaction are given in table 4. In order to refer the quantities of gaseous products back to the partial pressures which they exerted in the reaction vessel, runs were made with the addition of definite amounts of nitrogen. Thus two runs at 150.8°C. with oxygen–aldehyde ratios of 1.16 and 1.35 gave the following results:

TABLE 4

The gaseous products of the reaction

TEMPERATURE	ALDEHYDE PRESSURE	OXYGEN-ALDEHYDE RATIO	O_2	CO_2	CO	$\frac{CO_2}{CO}$
degrees C.	*cm.*		*per cent*	*per cent*	*per cent*	
152	20.0	1.20	47	27	13	2.1
153	20.0	2.05	78	9	5	1.8
150	20.0	1.16	51	27	13	2.1
151	20.0	1.35	66	17	7	2.4
139	30.2	1.60	73	13	5	2.6
139	30.0	1.54*	55	34	4	8.5

* Reaction mixture allowed to stand at 139°C. for 15 hours.

(a) $1C_2H_5CHO + 0.98O_2 = 0.11CO_2 + 0.05CO + 1.00$ Condensable
(b) $1C_2H_5CHO + 0.87O_2 = 0.13CO_2 + 0.05CO + 0.94$ Condensable

Hence, from a material balance, we find that the condensable products consist of (a) $C_{2.84}H_6O_{2.69}$, and (b) $C_{2.82}H_6O_{2.43}$. On chemical grounds the most probable product is propionic acid. On the basis of the carbon above, this has the formula $C_{2.82}H_{5.64}O_{1.88}$. This leaves unaccounted for (a) $H_{0.36}O_{0.81}$, and (b) $H_{0.36}O_{0.55}$. If a small amount of complete oxidation occurred, it would result in an amount of water equal to the CO + CO_2, i.e., 0.16 and 0.18 H_2O, respectively. This is in exact agreement with the hydrogen unaccounted for above. We still have unaccounted for (a) $O_{0.63}$, and (b) $O_{0.37}$. This can obviously be accounted for by assuming the formation of some perpropionic acid. This would have the formula

$C_{2.82}H_{5.64}O_{2.82}$. If the excess oxygen were used in this way, we would have (a) 67 per cent perpropionic acid, and (b) 40 per cent perpropionic acid. The overall reaction is therefore

$$\begin{aligned}\text{(a) } & 1C_2H_5CHO + 0.98O_2 = 0.11CO_2 + 0.05CO + 0.16H_2O + 0.56C_2H_5COOOH \\ & \qquad + 0.28C_2H_5COOH \\ \text{(b) } & 1C_2H_5CHO + 0.87O_2 = 0.13CO_2 + 0.05CO + 0.18H_2O + 0.30C_2H_5COOOH \\ & \qquad + 0.46C_2H_5COOH\end{aligned}$$

The presence of acids in the condensable products was confirmed by carrying out a run at 150.8°C. and removing the reaction bulb. The bulb was then thoroughly washed with distilled water and the washings titrated with 0.05 *N* sodium hydroxide. The results indicated approximately 1 molecule of acid for each molecule of aldehyde disappearing, as required by the above scheme.

A similar experiment was then carried out, the washings being analyzed for per acids using a neutral solution of potassium iodide and titrating the liberated iodine with 0.05 *N* sodium thiosulfate. Approximately 50 per cent of the total acid was found to be per acid, again confirming the above scheme.

In addition to the above products, traces of esters were detected by their odor. It has previously been shown (2) that ethyl propionate is a product of the decomposition of perpropionic acid. The formation of this compound would be accompanied by the formation of carbon oxides and water in equal quantities, and hence necessitates no modification in the above calculations.

Hence the predominant reaction under investigation is

$$C_2H_5CHO + O_2 = C_2H_5COOOH$$

followed by the formation of propionic acid from the per acid, or from a reaction between the per acid and the aldehyde.

The effect of surface

Runs were also made in a bulb packed with short lengths of Pyrex tubing, so as to increase the surface–volume ratio to about six times its former value. It was found that the reaction process was completely altered in the packed bulb. Aging effects were noticed, but after the surface had reached a steady condition it was found that the reaction now led to a pressure increase of about 15 per cent. It therefore appears that the chain process in the empty bulb has been wholly or partially replaced by a heterogeneous reaction.

It has previously been shown that in the empty bulb the pressure after its initial decrease then slowly rose again. As shown by table 4, this increase in pressure was accompanied by the production of a large amount of carbon dioxide. Analyses of the products from runs in the packed bulb, where there was also a pressure increase, showed the same preponderance of carbon dioxide. It thus appears probable that the secondary process in the empty bulb is also a surface reaction.

Explosions

There was no evidence of any critical explosion limits. Increased temperature and aldehyde concentration caused a progressive increase in the rate without any sign of a discontinuity.

DISCUSSION

As shown above, the main reaction is the oxidation of propionaldehyde to the per acid, followed by the formation of propionic acid from the per acid. The formation of the per acid would lead to a pressure decrease of 100 per cent, while the formation of propionic acid would give 50 per cent. Both reactions must thus occur, since the observed pressure decrease is about 75 per cent, but they are not necessarily independent processes. This point will be referred to again later.

There is no doubt that the main process involved is a chain reaction. This is shown by analogy with other gaseous oxidation reactions, and also by the characteristic form of the differential equation expressing the rate.

The heat of activation is 15,400 calories. This is considerably lower than that corresponding to a bimolecular reaction proceeding at an equal rate in the same temperature range. This, however, is a quite common characteristic of a chain reaction, since the heat of activation is a composite one and includes the temperature coefficient of the chain length.

One common criterion of a chain process is the suppression of the reaction by packing. In this case little information can be obtained from the results in the packed vessel, since the course of the reaction is completely altered. It appears, however, that the deactivating effect of the walls is not very pronounced. This is shown by the reproducibility of the results, and by the fact that inert gases, including excess oxygen, have little influence on the rate.

The mechanism of the reaction

As we have seen the rate of the reaction is given by

$$-\frac{d(C_2H_5CHO)}{dt} = K(C_2H_5CHO)^2$$

On the basis of the Bodenstein scheme (1) for the oxidation of acetaldehyde we have

$$A = A^* \qquad (1)$$
$$A^* + O_2 = P^* \qquad (2)$$
$$P^* = A^* + O_2 \qquad (3)$$

$$\begin{array}{rcll} P^* + A & = & P + A^* & (4) \\ P^* + K & = & P + K^* & (4) \\ P^* + O_2 & = & P + O_2 & (5) \\ P^* & = & P \text{ (wall)} & (6) \end{array}$$

where A represents aldehyde, P per acid, and K a negative catalyst.

In the absence of a negative catalyst, this leads to

$$-\frac{d(A)}{dt} = \frac{K_1K_4\,(A)^2}{K_5(O_2) + K_6K_5^2}$$

This equation disagrees with the experimental results in that it ascribes a retarding effect to oxygen. The only way to avoid this would be to assume that $K_6K_5^2$ is very much greater than $K_5(O_2)$. This, however, is not here a valid assumption since it has been found that the wall effect (K_6) is small.

Any attempt ~~to get over this difficulty by making minor modifications~~ in the scheme is impossible. On the Bodenstein scheme the only fate of A* is to react with oxygen. Hence oxygen exerts no favorable effect on the chain propagation to balance its deactivating effect, and thus it will always appear in the denominator.

To avoid this difficulty it is necessary to make a fundamental alteration in the initiation step, as follows:

$$\begin{array}{rcll} A + O_2 & = & P^* & (1) \\ P^* + A & = & P + A^* & (2) \\ A^* + O_2 & = & P^* & (3) \\ P^* + O_2 & = & P + O_2 & (4) \\ P^* & = & P \text{ (wall)} & (5) \end{array}$$

The alteration made here is to abandon the assumption of independent activation of the aldehyde, and substitute the more usual idea of an initial bimolecular step. Whence we have

$$-\frac{d(A)}{dt} = K_1(A)\,(O_2) + K_2(P^*)\,(A)$$

Evaluating the concentrations of unstable intermediate substances by equating their rates of formation and destruction in the steady state, we obtain

$$-\frac{d(A)}{dt} = K_1(A)\,(O_2) + \frac{K_1K_2(A)^2\,(O_2)}{K_4(O_2) + K_5}$$

Neglecting K_5, since the wall effect is small, and dropping the first term, since the chain-starting step is negligible compared to the chain-carrying step, we have finally

$$-\frac{d(A)}{dt} = \frac{K_1K_2(A)^2}{K_4}$$

which agrees with the experimental results.

It has been previously mentioned that propionic acid is also formed. If this results from a secondary decomposition of the per acid, the formation of the per acid will be the rate-determining step, and the above equation will still hold.

It is, however, possible that propionic acid arises from the reaction of aldehyde and per acid, as an integral part of the chain process. If so, we can account for the observed concentration relationships by the addition to the above scheme of the following steps:

$$P^* + A = S^* + S \qquad (6)$$

$$S^* + A = S + A^* \qquad (7)$$

where S represents propionic acid. This leads to the final equation

$$-\frac{d(A)}{dt} = \frac{2K_1K_4(A)^2}{K_4}$$

which is again of the right form. It seems likely that this is the way in which propionic acid arises, since a straight decomposition of perpropionic acid does not normally yield propionic acid (2).

The oxidation of acetaldehyde

As mentioned at the outset, it was hoped that this work might throw some light on the oxidation of acetaldehyde. It turns out in fact that the propionaldehyde oxidation is essentially similar to that of acetaldehyde, but lacks most of its complications. Thus both give per acids as the primary product. Both are accompanied by a pressure decrease, followed by an increase in the later stages. Both reactions have a low apparent activation energy, and there is no doubt that they proceed by chain mechanisms.

In addition the concentration terms in the expression for the rate are strikingly similar for both. Thus the propionaldehyde reaction rate is proportional to the square of the aldehyde concentration and independent of that of oxygen, while the acetaldehyde reaction is proportional to $(\text{aldehyde})^{1.7}$, and independent of oxygen.

The objections to the Bodenstein mechanism outlined above apply with equal force to the acetaldehyde oxidation. In view of the great similarity of the two reactions there is little doubt that they proceed by analogous mechanisms. It is therefore suggested that the scheme outlined above applies also to the main chain process in the acetaldehyde oxidation.

The acetaldehyde oxidation, however, is complicated by a pronounced induction period. A similar effect is noticed in the propionaldehyde oxidation in the first few runs in a new reaction vessel. When the walls have aged (presumably owing to irreversible adsorption of products), the induction period practically disappears. It is apparent therefore that the induction period with acetaldehyde may be explained by assuming that poisoning of the walls is a necessary preliminary to the propagation of chains.

SUMMARY

The kinetics of the oxidation of gaseous propionaldehyde have been investigated from 120°C. to 170°C. by a static method. The reaction is a chain process and is similar to the oxidation of acetaldehyde. The rate is proportional to the square of the aldehyde concentration, and independent of that of oxygen. The apparent heat of activation is 15,400 calories per gram-molecule.

The following mechanism is suggested for the oxidation of aldehydes:

$RCHO + O_2 = RCOOOH^*$ (1)
~~$RCOOOH^* + RCHO = RCOOOH + RCHO^*$~~ (2)
$RCHO^* + O_2 = RCOOOH^*$ (3)
$RCOOOH^* + O_2 = RCOOOH + O_2$ (4)
$RCOOOH^* = RCOOOH$ (wall) (5)
$RCOOOH^* + RCHO = RCOOH^* + RCOOH$ (6)
$RCOOH^* + RCHO = RCOOH + RCHO^*$ (7)

In the absence of deactivation at the wall, this leads to

$$-\frac{d(RCHO)}{dt} = \frac{2K_1K_6(RCHO)^2}{K_4}$$

in agreement with experiment.

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A STUDY OF THE INFLUENCE OF CAPILLARITY ON THE MELTING POINT OF IODINE[1]

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Received April 26, 1934

This study was undertaken with a view to accumulating additional evidence to support the capillary theory of adsorption (7). It was thought that support of the theory might be gained by the study of the adsorption of substances above and below the melting point. The reasoning was as follows: Above the melting point the adsorbed material would be in the liquid state and consequently the probability of its wetting the adsorbent would be greater than if it were in the solid state. If wetting occurred, then the curvature of the adsorbed material in the minute pits or capillaries of the adsorbent would be such as to produce a decrease of vapor pressure due to the tendency of the free surface energy to assume a minimum value. From this reasoning, it would be expected that the adsorption of vapors should increase at the solid-liquid transition point of the material adsorbed. In other words, the adsorption isotherm should exhibit a decided break in the curve at or above the melting point of the adsorbate.

The next question raised was that concerning the melting point of substances in small capillaries. Inasmuch as capillarity greatly influences the vapor pressure of highly curved surfaces, it follows immediately that the melting point must also be different in such a state than it is in bulk. These questions have been treated in detail in a later section of this paper. In this connection it is interesting to note that a recent paper by Kubelka (4) discusses this same subject. This article came to our attention after the completion of our experimental work.

Studies on solid adsorption (3) in which the adsorbent was kept well below the normal melting point of the substance adsorbed have been conducted in this laboratory. In the present work the adsorbent (silica gel) was kept below and above the normal melting point of the substance (iodine) adsorbed.

In order to facilitate the measurements a quartz fiber balance which has been described by McBain and Bakr (6) and by Cameron (1) was employed.

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[1] From the dissertation submitted by W. E. Land to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

APPARATUS

The apparatus used in these measurements is represented diagrammatically in figure 1. The balance and gel were contained in a large glass tube, A, mounted in an air thermostat, T. A glass support, B, having sealed-in iron rods, on which the platinum bucket containing the gel rested, could be raised and lowered by means of a solenoid. This device was used so that the gel could be activated at rather high temperatures without affecting the balance. One hook of a small cylinder, C, supported the fiber balance, while the other was used for lowering in place with the aid of a thread or wire.

A second air thermostat, T′, contained the substance to be adsorbed in a 50-cc. flask, D. The purpose of a similar flask, E, will be explained later. The glass tubing connecting tube A with flask D was wrapped with nichrome wire and heated electrically to prevent condensation of vapors. For the same reason it was also heated from the thermostat, T, to constriction, f. This tubing contained an inner seal, G, which was broken at the proper time by a small pointed glass tube containing a sealed-in iron rod. The latter was raised to a suitable height by a magnet and allowed to fall on the seal. The side arms, F and H, were constricted so that they could be readily sealed from the pumps. Omission of stopcocks from the essential parts of the adsorption apparatus was necessary for two reasons: (1) continuous heating of glass; (2) action of vapors on grease. A trap, I, surrounded with a mixture of ether and dry ice, was inserted between the parts to be evacuated and the U-tube, J. This trap prevented the diffusion of foreign vapors and allowed the iodine to be distilled from the flask D to the trap I. In this manner the vapor of this substance could be swept through the apparatus.

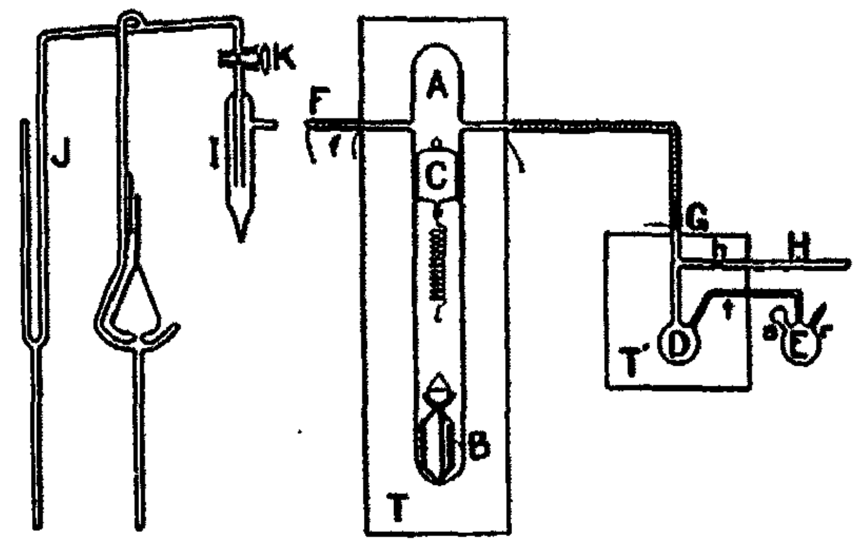

Fig. 1. Apparatus Used

The temperature of thermostats T and T′ (figure 1) was automatically controlled within ±0.2°C. by a mercury regulator and heating unit.

Thermometers used for both thermostats were calibrated. A motor-driven stirrer produced the necessary circulation.

The dimensions of the spring used in this work were as follows: average diameter of fiber, 0.010 in.; diameter of coils, 2 cm. The number of coils was twenty-seven. To relieve any strains, this spring, with an added load of about 0.5 g., was annealed for three days at 280°C.

The container for the adsorbent and also for the weights used in the calibration was made from platinum foil 0.0005 in. in thickness. This foil was made into a small bucket, the handle of which was No. 32 platinum wire. The finished bucket weighed 0.28+ g.

Preliminary experiments were conducted to determine whether there was any reaction between the platinum foil and the substance (iodine) adsorbed. Under the experimental conditions no appreciable reaction was detected.

The balance was calibrated over a period of one month at temperatures which covered the experimental range, and the initial and final calibrations were within experimental error. Since the cathetometer used for measuring the extension of the balance could be read to within 0.03 mm., differences in weight of 0.1 mg. could be estimated.

A McLeod gauge, with which pressures of 10^{-6} mm. could be read, was used to determine the degree of evacuation before sealing. Two mercury diffusion pumps, connected in series, and an oil pump, with suitable traps, were used in all cases to obtain a high vacuum.

EXPERIMENTAL

Commercial silica gel, the particles of which were of uniform size, was selected and purified in the following manner. The gel was treated with concentrated nitric acid and heated, with constant stirring, to the boiling point. The nitric acid was poured off after the gel settled. This was repeated several times to remove large foreign particles. It was then refluxed with concentrated nitric acid for three days, washed with distilled water for several days, and dried in an oven at 110°C.

Mercury used for the McLeod gauge, etc., was carefully cleaned and distilled. Chemically pure iodine was further purified according to the method of Lundell, Hoffman, and Bright (5).

The purified gel, contained in an evaporating dish, was partially activated by placing it in a cylindrical furnace continuously heated to 320°C. A stream of nitrogen gas, dried with sulfuric acid and calcium chloride, was passed over the heated gel for two days. About 0.5 g. of this gel, weighed in the platinum bucket, was lowered on support B (figure 1) into a long glass tube, A, having two small side arms. The balance hanging on the support C was next lowered in place and the top of A closed. Connections with this tube were then made as shown in figure 1.

The system was evacuated to the inner seal, G, through side arm, F.

During this evacuation the gel was heated to about 350°C. by a small cylindrical furnace. Since it is very necessary to remove permanent gases, all glass tubing was continuously heated at temperatures higher than those at which adsorption isotherms were run. Evacuation and activation of gel usually required from three to five days. The McLeod gauge showed the pressure to be 5×10^{-6} mm. of mercury before constriction f was sealed.

In order to remove moisture before the introduction of iodine, the remainder of the system was baked and evacuated through the side arm H. This part of the system was then disconnected from the pumps by closing stopcock K. To exclude moisture, capillary r was broken through rubber tubing connected with two calcium chloride towers. A thin glass bulb on the side arm s was next broken and an excess of pure dry iodine quickly introduced into flask E. After having sealed both capillary r and side arm s, flask D was surrounded with dry ice. To remove permanent gases, the pumps were kept running while the iodine was being distilled. By gently heating E with an incandescent lamp, this distillation required about four hours. Flask E was then sealed off at constriction t, and the evacuation continued for several days. With the McLeod gauge showing about the same pressure as above, constriction h was sealed.

The bucket containing the gel was then hung on the balance and the weight of activated gel obtained from the extension it produced.

After the thermostat containing the gel was brought to the desired temperature and the iodine was surrounded with a mixture of ether and dry ice, the inner seal, G, was broken. There was no weighable adsorption at this temperature. The influence of the variation in the pressure of the iodine upon the amount of adsorption was studied by varying the temperature of the iodine. The iodine was first surrounded with a mixture of ice and water. Higher temperatures, chosen to give suitable points on the adsorption curves, were obtained by means of thermostat T′. In order to prevent ordinary distillation of the vapor, it is always necessary to keep the gel at a slightly higher temperature than the iodine.

Values given in the literature (2) enabled a vapor pressure-temperature curve to be plotted, from which the pressures of iodine at these temperatures were obtained.

Before each run the system was reëvacuated and the gel activated. This was accomplished by renewing the side arm F. It is not necessary to replace the broken inner seal, G, since the gel can be completely desorbed by surrounding the iodine with an ether-dry ice mixture. This arrangement also permitted iodine vapor to be swept through the system.

Adsorption isotherms were obtained at 70°, 92.5°, and 115°C. Immediately after the maximum adsorption was reached, for a particular run, the gel was desorbed by decreasing the temperature of the iodine. In each case, several values were obtained which agreed, within experimental error, with those for the adsorption process.

An isobar was obtained by keeping the temperature of the iodine constant and varying that of the gel. The vapor pressure of the iodine corresponding to this constant temperature was 17 mm.

The same sample of gel was used for these runs.

TABLE 1

Adsorption of iodine

p	x/m	p	x/m
mm. Hg		*mm.* Hg	
T = 70°C.; weight of gel sample = 0.5700 g.		T = 115°C.; weight of gel sample = 0.5700 g.	
0.03	0.0004	0.97	0.0014
0.471	0.0035	1.95	0.0030
1.03	0.0075	2.90	0.0039
1.50	0.0105	4.75	0.0060
2.16	0.0144	6.80	0.0077
2.95	0.0179	8.90	0.0102
4.31	0.0277	11.02	0.0126
Desorption		13.50	0.0158
2.16	0.0144	15.00	0.0170
1.03	0.0088	16.75	0.0189
0.03	0.0009	18.50	0.0210
		20.45	0.0236
		22.90	0.0268
		24.40	0.0280
		32.00	0.0360
		Desorption	
		20.45	0.0233
		15.00	0.0175
		8.90	0.0119
Run No. 2. T = 92.5°C.; weight of gel sample = 0.5700 g.		Run No. 3. T = 92.5°C.; weight of gel sample = 0.5700 g.	
1.03	0.0040	2.05	0.0072
2.05	0.0074	6.95	0.0202
2.90	0.0095	11.02	0.0316
4.60	0.0142	13.50	0.0385
6.95	0.0202	15.10	0.0453
9.75	0.0272	16.30	0.0561
11.02	0.0312	18.65	0.0702
13.10	0.0378	20.80	0.0800
14.85	0.0438	23.30	0.0982
15.00	0.0456	24.70	0.1105
16.95	0.0575	Desorption	
16.95	0.0596	16.30	0.0655
Desorption		11.02	0.0319
11.02	0.0316		
6.95	0.0204		
2.90	0.0102		

RESULTS

The results of this investigation are given in tables 1 and 2. In each table the column headed x/m gives the grams of adsorbed material per gram of gel and the column headed p gives the equilibrium pressure in millimeters of mercury.

TABLE 2

Adsorption of iodine

Pressure of iodine = 17 mm.; weight of gel sample = 0.5700 g.

T	x/m
degrees C.	
85	0.0930
92.5	0.0591
100	0.0368
115	0.0198
130	0.0114
137.5	0.0088

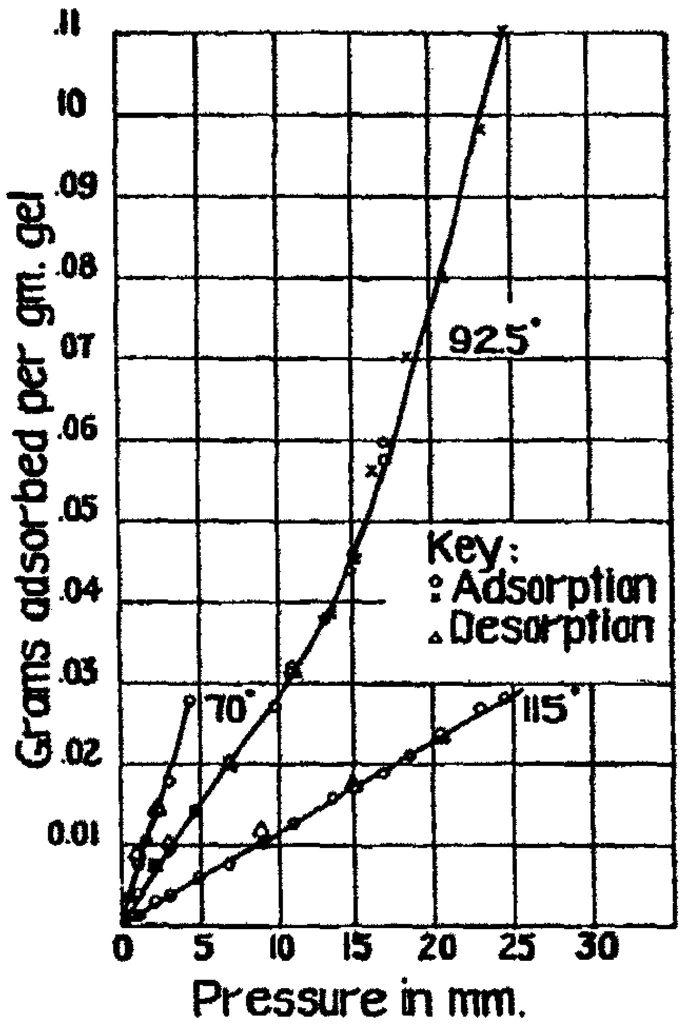

FIG. 2. IODINE ISOTHERMS

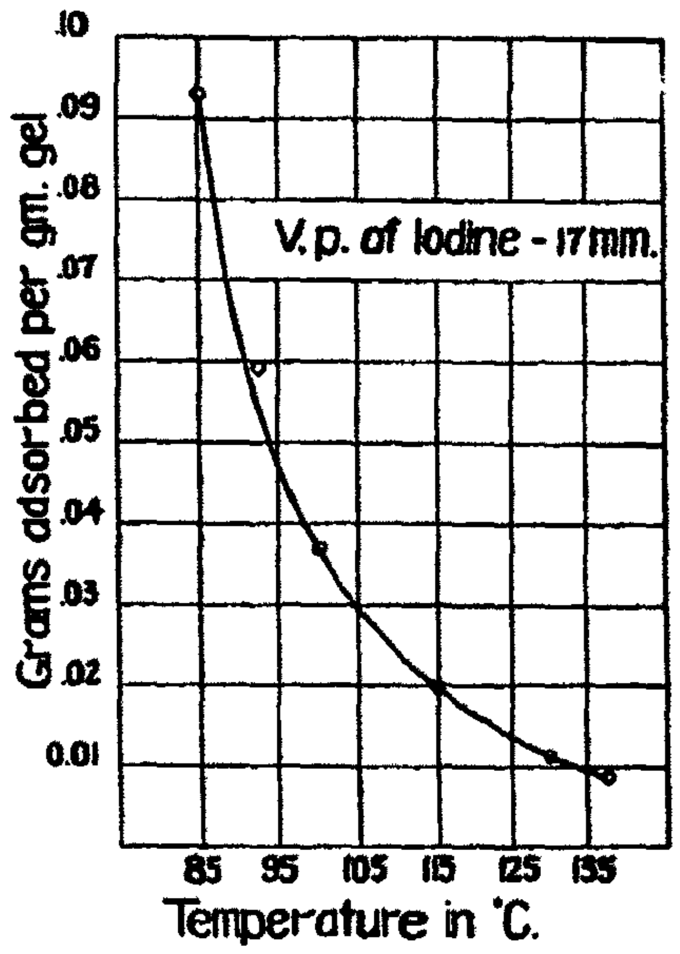

FIG. 3. IODINE ISOBAR

Table 1 gives the results for the three iodine isotherms at 70°, 92.5°, and 115°C., using the same sample of gel. In this way comparable results can be obtained. Figure 2 shows graphically the results of the first table. It is to be noted that a decided break in the curve of the 92.5°C. isotherm occurs at a pressure of about 11 mm. The curve of the 70°C. isotherm also bends noticeably upwards.

In table 2 are given the results of keeping the pressure of the iodine constant (17 mm.) and varying the temperature of the gel. These results are shown graphically in figure 3. This isobar is a smooth curve showing the normal behavior, i.e., a decrease in adsorption with an increase in temperature. The value of the water content of the gel was found to be 2.3 per cent.

DISCUSSION

The experimental work was performed in such a manner as to lead us to believe that we were in all cases dealing with true equilibrium phenomena. This criterion of real equilibrium is important, as so much erroneous adsorption theory has been drawn from faulty experimental data.

Our experiments show that the adsorption of iodine vapor decreases as we increase the temperature. This is normal behavior and is not in accord with the postulate that we proposed at the outset of this work. We expected to find an increase in the adsorption of iodine vapor above the normal melting point of iodine. However, we did observe a decided increase in adsorption in the case of the 92.5°C. isotherm when the pressure of the iodine exceeded 11 mm. We shall limit our discussion to this isotherm, inasmuch as experimental conditions made it possible for us to work over a sufficient range of pressures only at this temperature. Our explanation of the increase of adsorption at 11 mm. pressure on the 92.5°C. adsorption isotherm is that, at this pressure and temperature, liquid iodine is present in the capillaries of the silica gel, notwithstanding the fact that the ordinary melting point of iodine is 21.5°C. higher. It is to be noted that our quantitative calculations must necessarily be clothed with considerable uncertainties, owing to our lack of knowledge of the physical constants of matter in the state of highly curved surfaces. In other words, it is not safe to assume that the density, surface tension, or latent heat of vaporization of liquids in very small capillaries are the same as the normal values.

Let us consider the case of solid iodine in contact through the vapor phase with liquid iodine wetting a small capillary. The problem is to find the temperature at which the two phases of iodine have the same vapor pressure. It is known that the surface energy of the liquid iodine will operate in such a manner as to reduce the vapor pressure of the liquid. Consequently, the temperature of the solid iodine must be reduced below the normal melting point (114°C.) in order to maintain equilibrium. If we assume that the solid iodine is not affected by capillary forces while the liquid iodine is, the thermodynamic treatment is as follows:

The change in free energy of the solid and liquid (denoting the states respectively by the subscripts s and l) is,

$$dF_s = \left(\frac{\partial F}{\partial T}\right)_p dT = -S_s dT$$

$$dF_l = \left(\frac{\partial F}{\partial T}\right)_p dT + \left(\frac{\partial F}{\partial p}\right)_T dp$$

$$= -S_l\, dT + V_l\, dp$$

At the melting point $dF_s = dF_l$. Here dp is the change in the hydrostatic pressure on the liquid and we shall denote it by $d\pi$,

$$V_l\, d\pi = (S_l - S_s)\, dT$$

$$V_l\, d\pi = \frac{L_F}{T}\, dT$$

Integrating this expression between the limits π_1 and π_2 and T_1 and T_2,

$$V_l\,(\pi_2 - \pi_1) = L_F \ln \frac{T_2}{T_1}$$

In other words, we are able to calculate the temperature to which the system must be lowered in order to maintain equilibrium when the liquid iodine is under a known pressure.

We are also able to calculate the pressure under which the liquid iodine finds itself, owing to the action of the capillary forces, by making use of the well-known thermodynamic equation of Gibbs,

$$\frac{dp}{d\pi} = \frac{v}{V}$$

which expresses the variation of the vapor pressure p, with the hydrostatic pressure π, in terms of the specific volumes of the liquid v, and the vapor V. In our case the anomalous behavior begins at a pressure of 11 mm. and at a temperature of 92.5°C. Inasmuch as the following calculations are only approximate and as we wish to make sure that we are actually dealing with liquid iodine in the pores rather than with a monomolecular adsorbed layer which represents the phenomenon during the first stages of the adsorption, we have selected 20 mm. as the equilibrium pressure in our calculation. Before we can calculate the lowering of the vapor pressure of liquid iodine produced by capillarity, we must first know the vapor pressure of liquid or supercooled iodine at this temperature. This can be found by an extrapolation of the vapor pressure curve of liquid iodine or by means of the Clausius–Clapeyron equation. By neglecting the molal volume of the liquid by comparison with the molal volume of vapor and by assuming the vapor to be an ideal gas, the integrated form of this equation is,

$$2.3 \log \frac{p_2}{p_1} = \frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Assuming the normal value for the latent heat of vaporization, 10,500 cal. per mole (International Critical Tables), and substituting the following values in the above equation,

$$p_1 = 90.1 \text{ mm.} \qquad T_1 = 114° + 273° = 387°\text{K.}$$
$$T_2 = 92.5° + 273° = 365.5°\text{K.}$$

it is calculated that liquid iodine at 92.5°C. would have a vapor pressure of 39.8 mm. Extrapolation of the vapor pressure curve of liquid iodine gives the same value. Therefore the lowering of the vapor pressure amounts to (39.8 − 20) or 19.8 mm. Substituting the values,

$$p_2 - p_1 = -19.8 \text{ mm.} \qquad v = \frac{254}{4.0} = 63.5 \text{ cc. per mole}$$

$$\pi_1 = 0$$

$$V = \frac{RT}{p} = 11.4 \times 10^5 \text{ cc. per mole}$$

in the integrated form of the Gibbs equation,

$$p_2 - p_1 = \frac{v}{V}(\pi_2 - \pi_1)$$

gives a negative hydrostatic pressure, π, of 470 atmospheres. To obtain this value, we assumed the density of the liquid iodine in the small capillary to be the same as that of liquid in bulk.

If this approximate value of the negative capillary pressure (470 atmospheres) is now substituted in the equation connecting melting temperature with pressure as previously developed, and where

$$\pi_1 = 0 \qquad V = 63.5 \text{ cc. per mole}$$
$$\pi_2 = -470 \text{ atmospheres} \qquad L_F = 4000 \text{ cal. per mole (I. C. T.)}$$
$$T_1 = 114 + 273 = 387°\text{K.}$$

a melting temperature $T_2 = 323°$K. or 50°C. is obtained. A lowering of the melting point of iodine of 64°C. (114°C. − 50°C.) is indicated.

These calculations lead us to the conclusion that we are completely justified in our contention that it is possible for liquid iodine to exist in a capillary tube in which the vapor pressure of the liquid is only 20 mm. We have seen that our calculations would lead us to the conclusion of a lowering of the melting point of 64°C. This calculated value of the melting point lowering cannot be considered as accurate, owing to our lack of knowledge of the proper value of the physical constants of liquid iodine in capillaries. We have assumed, for example, the normal density of liquid iodine in the capillaries; this is certain to be incorrect, inasmuch as the very nature of the change in vapor pressure produced by pressure is predicated upon a change in density of the condensed phase.

We have shown that it is possible for the liquid state to have a stable existence far below the normal melting point, provided sufficiently powerful capillary forces are in operation. It is evident that these forces must diminish in magnitude as the adsorption increases, i.e., as the pores fill it is necessary to assume increasing radii of curvature. Therefore, it is necessary to assume the existence of unstable liquid at some point higher on the adsorption isotherm.

SUMMARY

1. Measurements have been made of the adsorption of iodine vapor by silica gel at three temperatures.

2. The adsorption isotherm of iodine at 92.5°C. showed a pronounced flex upwards when a definite pressure was reached.

3. The above behavior was explained by the assumption of liquid iodine being present in the silica gel and wetting the walls of the same.

4. The effect of free surface energy on the solid-liquid transition temperature was thermodynamically explained.

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THE ACTION OF WATER ON THE LATENT PHOTOGRAPHIC IMAGE

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Received June 27, 1934

If considerable intervals elapse between the exposure and development of a photographic emulsion kept in a warm humid climate, a flat image is usually obtained. Strauss (5) suggested that water vapor might be the cause of this lack of contrast, and gave experimental evidence to support his view.

The present paper deals with the rôle of water in the above effect.

DESTRUCTION OF LATENT IMAGE BY WATER VAPOR

We have observed that if an Azo emulsion (commercial Azo paper) is exposed to light so as to produce considerable but not maximum developable density, the latent image is either completely destroyed, or reduced to a normal reflection density of less than 0.2 (the actual final value of the density is dependent upon the initial density) by storing the emulsion for several hours in an atmosphere saturated with water vapor at 20°C. The emulsion thus treated is, when dry, capable of yielding very satisfactory prints after a second exposure to light.

In order to eliminate the possibility that some substance other than water vapor was producing the effect, plates coated with an Azo emulsion were stored from twenty-four to forty-eight hours *in vacuo* at a pressure well below 1 mm. They were then exposed to light passing through the walls of the container, and water vapor was introduced by breaking within the container a sealed bulb filled with freshly distilled water. No appreciable difference was noticed in the time required to reduce the latent image to a minimum developable value in the above case than in a similar experiment carried out in the presence of air. A control, stored for forty-eight hours *in vacuo*, exposed as before, and developed, showed that the vacuum storage did not appreciably alter the sensitivity of the emulsion.

Much longer periods of treatment with water vapor are required to destroy latent images (reduced to a developable density of less than 0.2) existing in bromide papers: Eighty hours at 25°C. were required to destroy a latent image produced upon enlarging paper by full exposure to light. An even longer period was required by bromide emulsion film. Slow Eastman process film, given normal exposure to light, showed a marked reduction in density after one hundred and forty-four hours in a saturated atmosphere at 25°C. but complete destruction of the latent image was not effected.

The results of an investigation of the destruction of the latent image by other agents suggests a possible explanation for the action of water vapor. Ether, ethanol (absolute), carbon tetrachloride, carbon disulfide, benzene, and nitrobenzene are without appreciable effect in the vapor phase. Formic and acetic acid vapors and liquid ethylene glycol, however, are even more effective in destroying the latent image than water and, as with the latter, this destruction of the light impression has no effect upon the sensitivity, provided that the treatment is not prolonged beyond the point of complete destruction.

Since the agents found to be effective in destroying the latent image in the same manner as water are of widely different chemical properties, it seems improbable that the effect is chemical in nature. One physical property common to all the effective agents is, however, their ability to soften gelatin in the same manner as does water. Every one of the limited number of substances tried which was without softening action upon the gelatin was likewise without the above effect upon the latent image.

The evidence indicates, accordingly, that the destruction of the latent image by water and by the organic compounds of analogous action is in effect the reverting of the exposed grains to a state not differing greatly (at least photographically) from the original unexposed condition of the grain. The softening of the gelatin greatly facilitates a preëxisting tendency towards reversal of the exposed grain.

Photographic theory assumes that the process of exposure results in the liberation of silver and halogen in equivalent quantities. The liberated halogen is taken up by a "halogen acceptor" which prevents reversal, at least in some measure. Kieser (3) has shown that in the exposure of pure silver bromide grains, reversal predominates to such an extent that a quantum yield of only 1/15th is obtained, whereas in the presence of a suitable acceptor the quantum yield approaches unity. In the case of the usual gelatin emulsion Germann and Hylan (2) have shown by quantitative experiments that gelatin itself probably plays the rôle of the halogen acceptor. A more active acceptor than gelatin might be expected to prevent reversal even by water, and such is found to be the case. Azo F No. 2 paper, soaked for 5 minutes in a solution containing 1 per cent silver nitrate and 1 per cent citric acid, produced upon exposure a latent image which was incapable of destruction by water vapor in the usual way. Moreover, solio paper, in which an excess of silver nitrate again acts as a powerful acceptor, yields upon exposure in the normal manner an image which cannot be destroyed by water-vapor treatment.

When Azo F No. 2 paper, exposed to strong sunlight until highly colored, was treated with water vapor for several hours, the color practically disappeared and only a small density was obtained upon development. This paper was capable of producing an image upon a second exposure, although its speed was reduced by about one-third. When, however, the exposed paper was bathed for 5 minutes in liquid water (which Kieser found to be a suitable halogen acceptor), then dried rapidly and treated with water vapor as before, no decrease in developable density was produced.

Measurements of the time rate of destruction of the latent image (by water vapor of constant pressure) indicate a reaction of the first order.

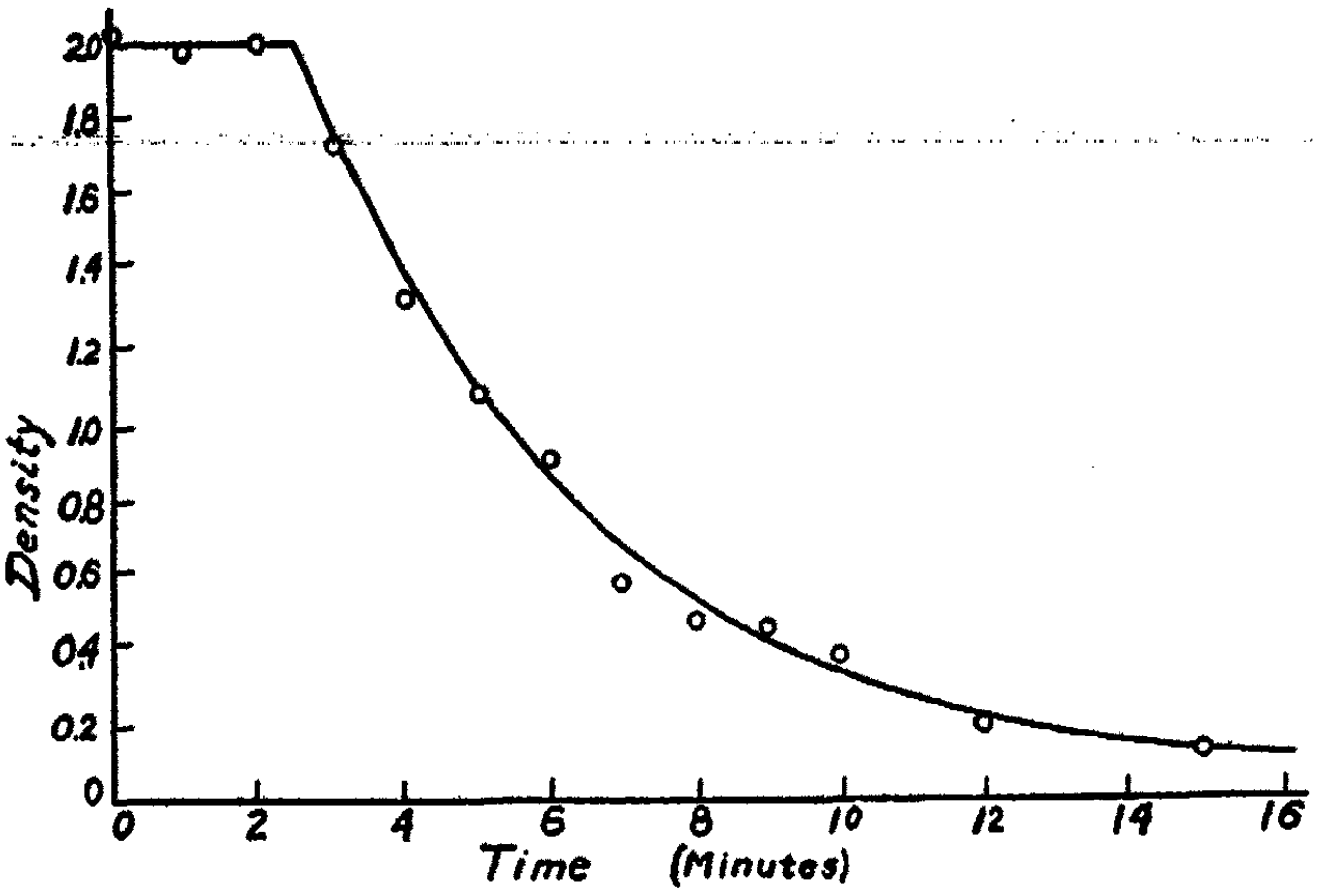

FIG. 1. THE TIME RATE OF DESTRUCTION OF THE LATENT IMAGE BY WATER
The solid line is the theoretical curve

For this investigation Azo No. 1 emulsion coated on glass was used. The data fall very well upon the curve given by the equation

$$X - X_0 = X_m e^{-k(t-t_0)} \tag{1}$$

where X is the density (transmission) at any time t, X_0 is the density when $t = \infty$, X_m is the initial density, t_0 is the time required for the water vapor to penetrate and soften the gelatin, and k is the reaction constant.

The smooth curve of figure 1 is the theoretical curve given by the above equation when $X_0 = 0.05$, $X_m = 2.00$, $t_0 = 2.5$ minutes, and $k = 0.255$.

This equation would be in harmony with the assumption that the water vapor acts chemically upon the development centers of the exposed grains, rendering them undevelopable, provided we could assume that the concentration of the water vapor remained constant at the center in question. This assumption, however, would have to be justified. Moreover, if this were the case, we should expect *complete* destruction of the image, regardless of the amount of the initial light exposure. In reality, complete destruction is attained only if the light exposure is small, and the amount of residual density, although always small, increases with the period of exposure. This fact may be explained by the assumption that the greater the exposure, the greater the amount of halogen which has been definitely removed from the sphere of action. This escape of halogen also explains why it is impossible to destroy by water-vapor treatment the image due to age (age mottle).

The destruction of the latent image by water furnishes, perhaps, a partial explanation for the results of Sterry (4) and Cousin (1), who found that the moistened emulsion was less sensitive than the dry one.

THE SENSITIZING ACTION OF WATER

If unexposed Azo F No. 2 emulsion is treated with water vapor for several hours at 25°C. and then dried, the sensitivity of the emulsion is increased. The longer the wave length the more marked is the effect. If the emulsion is first exposed to light so as to produce a high developable density and then treated with water vapor to destroy the image, the sensitivity on second exposure is about the same as that of the water-treated, unexposed emulsion. Figure 2 shows the results of a typical experiment. The curve defined by the triangles is the density–exposure curve for an untreated emulsion. The circles represent the experimental points obtained with an emulsion which had been treated with water vapor for three hours at 25°C. and then dried. The curve defined by the crossed circles was obtained with an emulsion which had been exposed to light to give a near-maximum density, and then treated with water vapor as above. The density from the preëxposure was not completely destroyed by the water-vapor treatment, and an appreciable residual density remained. In order to correct for this, accordingly, it is necessary to shift the curve along the exposure axis until the point of residual density falls upon the normal exposure curve (not shown in figure) for the water-treated, not preexposed, emulsion. The curve thus obtained is shown by the broken line, which falls closely along the points of the water-treated, not preëxposed emulsion.

THE FOGGING ACTION OF WATER VAPOR

If Azo paper is exposed to saturated water vapor at 25–30°C. for several days, considerable developable density or fog is produced. This fog resembles very closely that due to age (age mottle). The action of various chemical agents on this water fog is the same as that of these agents on age mottle.

Further evidence that water vapor is intimately connected with the age deterioration of paper is given by the following facts. If Azo paper is washed free of soluble salts, the rate of spontaneous deterioration with age is increased to such a degree that a measurable developable fog appears after standing in air a few days. We have been able, however, to keep strips of such paper for weeks without fogging by storing them in a desiccator over phosphorus pentoxide, whereas strips of the same paper stored in air at the generally prevailing humidity yielded a normal reflection density of about 1 after a week.

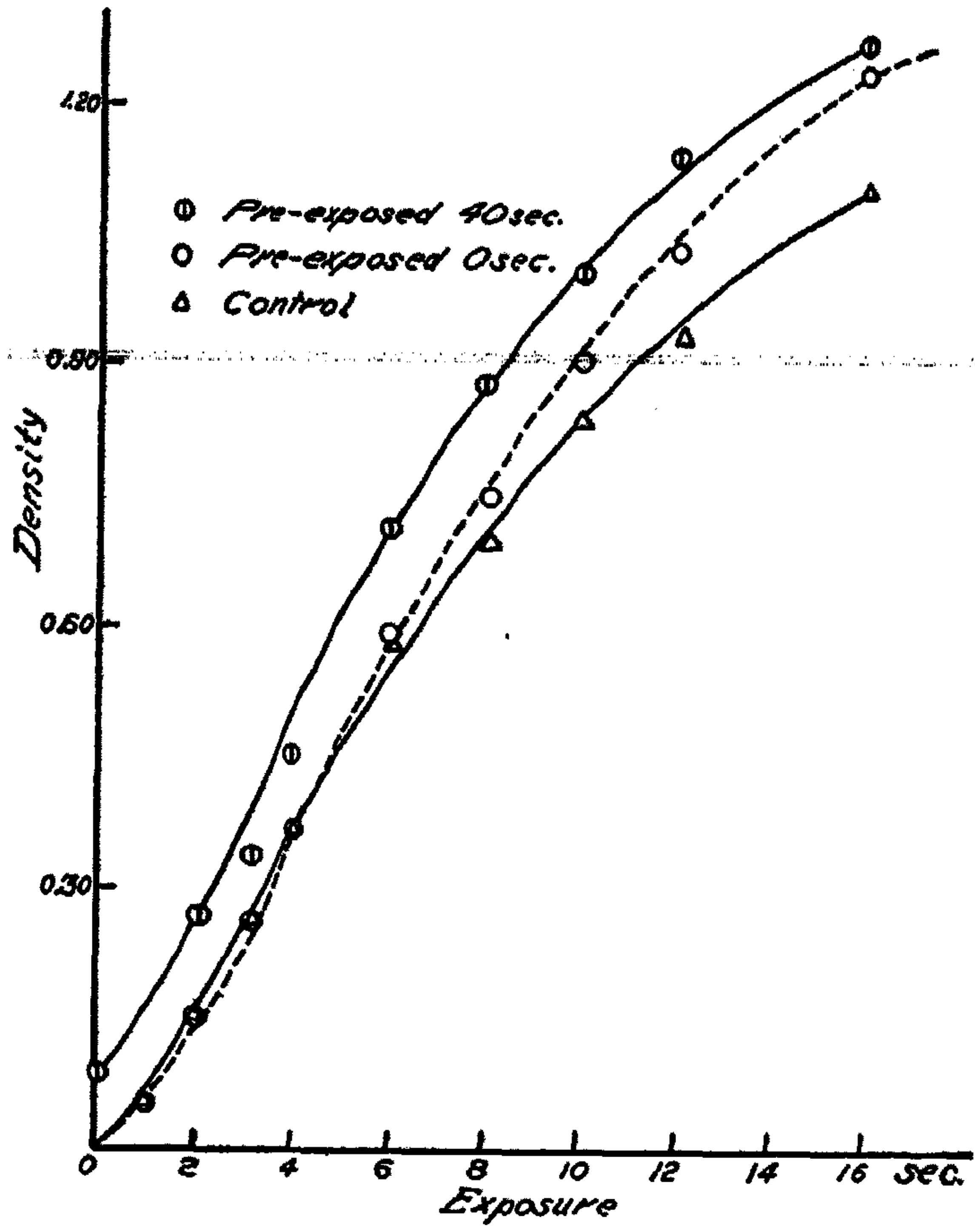

FIG. 2. THE EFFECT OF WATER ON THE SENSITIVITY OF AZO F NO. 2 EMULSION

SUMMARY

The phenomenon of the destruction of the latent image by various chemicals in the vapor phase has been investigated. Water vapor is shown to be very effective in destroying the latent image, but formic and acetic acid vapors and liquid ethylene glycol are found to be even more effective. Provided treatment is not carried to a point of complete destruction of the image, there is no consequent effect on the sensitivity. The vapors of ether, absolute ethyl alcohol, carbon tetrachloride, carbon disulfide, benzene, and nitrobenzene have no appreciable effect on the latent image. The very diverse chemical nature of the vapors capable of destroying the latent image would argue against a possible chemical action. The physical property of softening the gelatin similarly to water is common to all the effective agents. It is therefore suggested that the softening of the gelatin greatly facilitates a preexisting tendency toward reversal of the exposed silver halide grain.

It is shown that water vapor may serve as a sensitizer. Sensitivity is increased more for long than for short wave lengths in the case of Azo F No. 2 emulsion.

A definite relation between age mottle and the water vapor content of the atmosphere is shown to exist.

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No. 17.

THE VISCOSITY OF NITROCOTTON IN VARIOUS SOLVENTS AND MIXTURES

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Received May 3, 1934

A previous communication[2] (6) presented a systematic report upon the apparent viscosity of solutions of nitrocotton (12.10 per cent nitrogen) in a large number of solvents and solvent mixtures over periods of time up to one year. Many interesting and significant regularities appeared, of which three may be mentioned. (1) The best solvents give the least viscous solutions with the same nitrocotton, the viscosity being referred to that of the solvent itself in each case. (2) Mixtures are better solvents than pure liquids. (3) The apparent viscosity is largely due to a structural effect,[3] since it is altered by shaking, change of solvent, previous treatment, previous precipitation and recovery of the nitrocotton, and because of its enormous magnitude. All this is additional to any effect of the length of the molecule itself, so much stressed in subsequent years by Staudinger and others. The effects quoted above cannot reasonably be ascribed to alteration in the length of the molecule itself, more especially since changes occur in both directions.

Many questions demanding further study arose, some of which are dealt with in the present report.

EXPERIMENTAL METHODS

The nitrocotton "1919" has been described, together with the method of drying, storage, and preparation of the solutions (6). Units of weight,

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[1] The experiments were performed by E. M. G. except where otherwise noted. The work was carried out at Bristol University, England, during the years 1925–27.

[2] The following errata in this article should be noted: p. 321, table V, for methyl phenyl urethane (Smith) the time of standing should be 3.2 hours instead of 32; p. 325, table VII (last column), the slope should be 0.344 instead of 5.589 (this is not a fair comparison as the concentration is so great); p. 326, figure 3, on the figure itself "phenol urethane" should be "phenyl urethane," in the title of the figure "phenyl methane" should be "phenyl urethane" and "ortho tolyl methane" should be "benzyl phenyl urethane"; p. 330, table XI, the viscosity of pure ethyl phthalate (Nobel's; December, 1923) should be 0.04215 instead of 0.4215; p. 333, third line from the bottom, "less impure" should be "less pure."

[3] This was developed as a general explanation of the high viscosity of numerous colloids by J. W. McBain (J. Phys. Chem. 30, 239 (1926)).

volume, temperature, viscosity, etc. were corrected to absolute standards. Viscosity determinations at 25°C. were exactly as at 55°C., except that the time at 55°C. was 23 hours and 10 minutes before cooling to 25°C. Viscometers were chosen of dimensions to give absolute viscosities with true liquids of the same apparent viscosity as the actual nitrocotton solutions. The results are usually the mean of independent duplicate experiments.

VISCOSITY IN A SERIES OF ACETATES AS SOLVENTS

In the previous communication (7) it was indicated "that molecular weight is an important factor in a series of closely similar compounds. The lower the substance in the homologous series the better the solvent." Also aliphatic substituents appear more favorable than aromatic. One expects the greatest differences with the lowest homologues. These rules appear to obtain with the acetates, although the lowest homologues could not be dried with calcium chloride and were too impure.

It has already been emphasized that impurities greatly affect and generally improve solvent power. Hence for comparison the solvents should be of comparable purity and dried in similar fashion. Otherwise, divergent values are obtained. For example, the solvents were dried with calcium chloride or copper sulfate. The latter, however, introduced a further impurity, presumably sulfur dioxide, which lowered the viscosity, as did sulfur dioxide, the viscosity rising again upon removal of the sulfur dioxide. For example, with isobutyl acetate, the viscosity 0.00643 became 0.00636 after treatment with copper sulfate; 0.00632 after copper sulfate and carbon dioxide; 0.00543 after sulfur dioxide, and 0.00630 after removing most of the sulfur dioxide. Similarly, with isoamyl acetate, 0.00793 became 0.00799 after drying with calcium chloride, and 0.00791 after drying with calcium chloride and copper sulfate.

The solutions were prepared at 55°C. and measured at age 24 hours at 25°C. The data are calculated as in the previous communication, that is, the logarithm of the ratio of the viscosity of a solution to that of the solvent contained therein is divided by the concentration expressed in grams of nitrocotton per 100 grams of solvent. This gives the slope of the graph of the logarithm of the relative viscosity against the concentration, which is, as a first approximation, a straight line. The results are collected in table 1. The source of solvents is indicated as follows: K = Kahlbaum, N = Nobel's, B.D.H. = British Drug Houses, E.K. = Eastman Kodak Co., M = Merck. Purest solvents obtainable from each source were redistilled.

It follows from table 1 that the higher homologues under similar conditions have a value 1.75 ± 0.05. This does not include the aromatic derivative, phenyl acetate, a poorer solvent as indicated by its higher slope, but it does include benzyl acetate with its interposed CH_2 group. Methyl, isopropyl, and butyl acetates are among the most highly sorbed of volatile solvents, x/m, the sorption expressed in grams, exceeding unity for high relative pressures (5). The number of molecules taken up is greatest for methyl and least for butyl acetate.

TABLE 1

Mean viscosity slopes ($\log \eta/\eta_0 \div$ per cent) of approximately 0.5 per cent (grams nitrocotton per 100 grams solvent) nitrocotton in various solvents dried and undried

Prepared at 55°C.; measured at 25.00°C.; age 24 hours

SOLVENT	MEAN VISCOSITY SLOPES		
	Untreated	Dried with $CuSO_4$	Dried with $CaCl_2$
Methyl acetate (K)	1.44	1.12	
Ethyl acetate (K)	1.55		
~~Ethyl acetoacetate (N)~~	~~0.778~~		
Propyl acetate (K)	1.06		1.72
Isopropyl acetate	1.09	0.832	
n-Butyl acetate (K)		1.05	
Isobutyl acetate (K)	1.16	1.18	1.72
Isoamyl acetate (B. D. H.)	1.16	1.41*	1.77
Benzyl acetate (K; May, 1925)	1.24		
Benzyl acetate (K; March, 1926)	1.66		1.79
Benzyl acetate (K; November, 1926)			1.82
Phenyl acetate (K; May, 1925)	1.92		1.94
Phenyl acetate (K; March, 1926)	2.34		2.35
Phenyl acetate (K; November, 1926)			2.20

* Dried with calcium chloride and then copper sulfate.

TABLE 2

Mean viscosity slopes of approximately 0.5 per cent nitrocotton in solvents at 25°C. and 55°C.

SOLVENT	MEAN VISCOSITY SLOPES		
	At 25°C.	At 55°C.	At 55°C.*
Ethyl acetoacetate (N)	0.778	0.952	0.91
Methylphenylurethan (N; February, 1925)	1.69	1.41	1.61
Ethylphenylurethan (N; February, 1925)	1.58	1.54	1.80
Diethyl carbonate (N)	1.87	1.52	1.58

* Previous communication; different specimens of solvent.

To compare the results in table 1 for acetates too volatile to measure at 55°C. with the solvents previously studied at this temperature, the data in table 2 for solutions at both temperatures are assembled.

It will be noted from the low value of the slopes that the acetates would be classed as good solvents, with the exception of phenyl acetate. For the last three substances in table 2, the slopes are higher at 25°C. than at 55°C. and the order in the three columns is not identical. This is partly because other samples of a different degree of purity were employed for the last column.

SOLUBILITY AND VISCOSITY IN ALCOHOLS

Methyl alcohol is almost a complete solvent. Ethyl alcohol is such only at very low temperatures, the solution becoming more viscous and setting to a jelly on warming to room temperature.[4] This reversible change cannot, of course, be ascribed to a change in the length of the molecule. Butyl alcohol is a non-solvent and it is sorbed to a far less extent by nitrocotton, not exceeding 5 per cent by weight.

The solubility and slope of nitrocotton were determined in Kahlbaum's ~~methyl alcohol; also in a sample of the latter which had been dried with~~ calcium chloride; also in dry ethyl alcohol and in a 50-50 mixture by weight of undried methyl alcohol and dry ethyl alcohol. In all cases nitrocotton solutions were prepared in the ordinary manner as for measurement at 25°C., but before the viscosity was taken any undissolved fibers were filtered off. Then a known weight of the filtrate was evaporated to constant weight. From this was calculated the percentage of the 0.5 g. of nitrocotton which had dissolved in the 100 grams of solvent. The nitrocotton was, of course, not uniform, and this affords a sensitive test of progressive dissolving power without measuring a true solubility in the ordinary sense. The data are given in table 3.

TABLE 3

Viscosity and dissolving power in methyl alcohol, ethyl alcohol, and in a mixture of equal weights, at 25.00°C. and age 24 hours

SOLVENT	NITRO-COTTON DISSOLVED	DECREASE	VISCOSITY SLOPE	DECREASE
	per cent	*per cent*		*per cent*
Methyl alcohol (K)	91.1		0.620*	
Methyl alcohol (K), dried with $CaCl_2$	85.2		0.654	
Ethyl alcohol	24.1		2.275	
Methyl alcohol (K) + ethyl alcohol	45.4	21	1.199	18

* At age 47 hours.

It will be seen from table 3 that, as was expected and in accordance with

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[4] C. W. Hutchinson in our laboratory finds that ether-alcohol (75:25) containing 5 per cent nitrocotton at room temperature forms an opaque gel on heating in a sealed tube to 90°C. The phenomenon is completely reversible, the gel quickly reverting to a fluid sol at room temperature.

our rules, drying[5] diminishes the solvent power of methyl alcohol, as shown both by the increased viscosity and the small proportion of nitrocotton dissolved. On the other hand, the mixture of the two alcohols yields a viscosity as well as a proportion of nitrocotton dissolved which is one-fifth less than that of the arithmetic mean of the two solvents separately.

HIGH MELTING SOLVENTS IN MIXTURES WITH ALCOHOL AND BENZENE

Since seven possible solvents are solid at 55°C., the attempt was made to study them at 55°C. in admixture with ethyl alcohol or benzene. Table 4 presents the results with alcohol. Equal parts by weight of benzene with phenylurethan or diethyl carbonate did not dissolve the nitrocotton. This was likewise the case with one part of phenylacetanilide and three parts of alcohol, and one part of α-pyridylurethan[6] with five parts of alcohol. Some substances previously measured in pure condition are included for comparison.

TABLE 4

Viscosity slopes of solutions of nitrocotton in substances to which an equal weight of ethyl alcohol has been added

Temperature, 55°C.; time, 24 hours

SOLVENT	SLOPE		PER CENT DECREASE
	Pure	Mixture	
Form-*o*-toluidide (N)	1.058	0.870	18
Phenylurethan (N)	1.340	1.04	22
Methylphenylurethan (N; February, 1925)	1.407	0.89	37
Diethyl carbonate (N)	1.524	1.08	29
Ethylphenylurethan (N; February, 1925)	1.535	0.94	39
Ethyl phthalate (E. K.)	1.611	1.27	29

It has already been pointed out that a small addition, even of a reputed non-solvent, lowers the viscosity and improves the solvent power of any solvent for nitrocotton. Thus at 55°C. even the extreme non-solvent hexane, added in one or two parts per hundred, lowers the actual viscosity slope of the solvent methylphenylurethan by 3 and 6 per cent.[7] Other examples are given in table 4. This is likewise shown in figure 1 for the effect of the semisolvent, ethyl alcohol, upon methylphenylurethan over

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[5] For solvents previously studied at 55°C., drying a solvent over phosphorus pentoxide for 14 days at room temperature raised the slope for benzylphenylurethan (N) 8 per cent, leaving that for methylphenylurethan (N; February, 1925), ethylphenylurethan (N; November, 1926), and diethyl carbonate (N) unaffected.

[6] α-Pyridylurethan is insoluble in benzene.

[7] An opposite effect is probably produced upon acetone.

the whole possible range. Beyond 85 per cent alcohol, progressively less of the nitrocotton dissolves, and the true slope cannot be measured, although it must become very high (cf. table 3).

For comparison with the mixtures in table 4 the following results were obtained with similar mixtures of high melting substances: diethyldiphenylurea (N), 0.677; phenyl oxamic ester (N), 1.136; *p*-toluenesulfonanilide (N), 1.110; diphenylurethan (N) (42 g. in 58 g. of alcohol), 0.849.

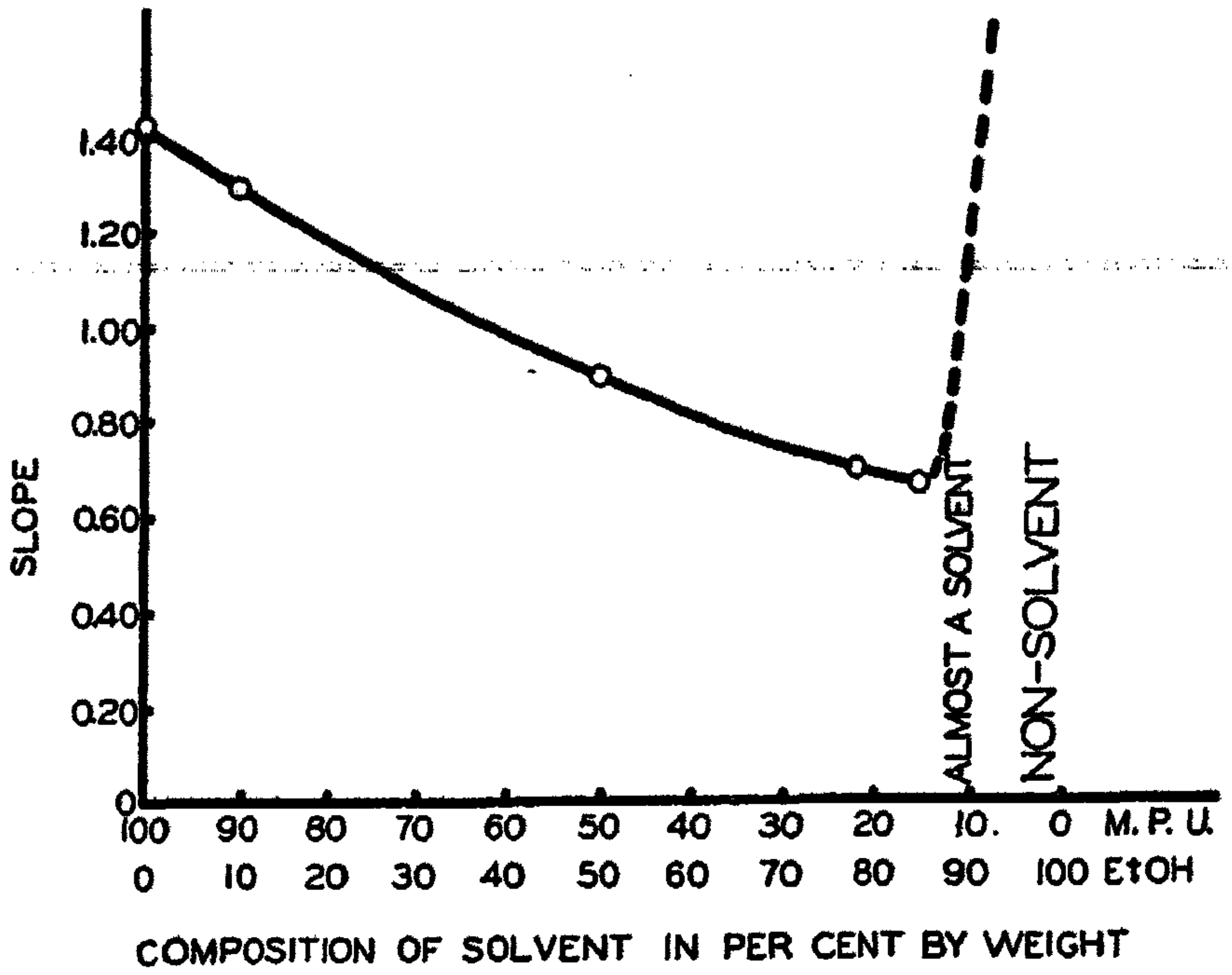

Fig. 1. Viscosity Slopes of 0.5 Per Cent Solutions of Nitrocotton in the Solvent Methylphenylurethan, to Which the Semisolvent Ethyl Alcohol is Added in Increasing Amounts, Lowering the Viscosity of the Mixture

Temperature, 55.00°C.; time, 24 hours

With benzene (K) mixtures containing equal parts by weight, the slopes for the mixtures were 0.953 and 1.66 for form-*o*-toluidide (N) and methylphenylurethan (N; February, 1925), respectively, being a decrease of 15 per cent for the former but an increase of 18 per cent for the latter. The slopes for 50 per cent mixtures of benzene (K) with diethyldiphenylurea (N), phenylacetanilide (N), and diphenylurethan (N) were 1.47, 1.45, and 2.10, respectively.

It follows from the data adduced that all are to be classed as good solvents except α-pyridylurethan and phenylacetanilide. These two are too insoluble even in alcohol and benzene to be given a comparable test. Further, it is to be remembered that the specimens of the high-melting solvents were in most cases not as pure as the standard solvents used for comparison in table 4. Lastly, the relative order is certainly affected by such large additions of alcohol or benzene.

Contrary to expectation, the data indicate that diphenylurethan is potentially a better solvent than phenylurethan.

Besides these and the numerous striking examples of the lowering of viscosity slopes in mixtures given on pp. 325 to 328 of the previous communication (6), three more may be cited; namely, that in table 3, and the 50 per cent mixtures of *n*- and isobutyl acetates (K), and of benzyl with phenyl acetate (K). The slopes for the last two mixtures at 25.00°C. were 1.384 and 2.009, being 13 and 10 per cent less than the means for the respective pure solvents. Further, 50 per cent mixtures of formanilide and form-*o*-toluidide yielded a slope of 0.985 at 1 day and of 0.074 at 80 days, being 7 per cent less than the mean of the values for the two solvents at 1 day, 1.02 and 1.085, respectively.

C. W. Hutchinson in the Bristol laboratory found that the addition of a few per cent of the following impurities did not cause the residue of nitrocotton particles left undissolved by specially purified formanilide (N) to dissolve: aniline (except in certain cases upon prolonged shaking), formic acid, ether, alcohol, 5 per cent ether-alcohol, formamide, benzene, toluene, tartaric acid, citric acid. On the other hand, 2 or more per cent of acetone was successful. Guncotton and another sample of nitrocotton dissolved in the same incomplete manner. Aniline and formic acid by themselves do not affect the appearance of nitrocotton.

PROLONGED PREHEATING OF SOLVENTS

Ethyl phthalate has given us much trouble throughout the many years in which we have studied solutions of nitrocotton therein. (See figure 4, page 335, of reference 6.) The first sample obtained was an excellent solvent with one of the lowest viscosity slopes. Subsequent much purer specimens have given high slopes.

Since in prolonged aging experiments at 55°C. it might be surmised that the solvent itself is changing, different specimens of two solvents were maintained at the very much higher temperature of 130°C. for 7 days in sealed tubes previously evacuated with a mercury pump with a trap containing solid carbon dioxide and ether or liquid air. Where necessary the liquid itself was surrounded by solid carbon dioxide and ether. *o*-Tolylurethan was partially converted to a form with a melting point higher than 130°C. as compared with the original melting point of 45°C. The results given in table 5 were obtained with 0.5 per cent solutions subsequently prepared, aged, and measured at 55.00°C. Each solution was in a separate sealed tube.

Viscosity is distinctly lowered by the previous drastic treatment of the triacetin. The effect is slight with phenoxyacetic ester. With ethyl phthalate a distinct increase results as shown in table 6.

A graph of all these slopes against the logarithm of time yields approximately straight lines, indicating that the viscosity of the solution would fall to that of the solvent after 600 to 800 days at 55°C. However, it is worth noting that during prolonged aging some of the nitrocotton definitely separates out from the ethyl phthalate solution. The solutions in triacetin and phenoxyacetic ester would seem to tend towards their end point in 300 to 500 days.

TABLE 5

Results obtained in preheated solvents

SOLVENT	VISCOSITY SLOPES				
	24 hours	14 days	42 days	84 days	168 days
Triacetin (N)*	1.225	0.890	0.626	0.373	0.174
Triacetin (N)†	1.023	0.511	0.324	0.226	0.124
Triacetin (K)*	1.230	0.874	0.508	0.362	
Triacetin (K)‡	1.025	0.759			
Phenoxyacetic ester (N)*	1.451	1.038	0.770	0.519	0.283
Phenoxyacetic ester (N)†	1.319	0.976	0.744	0.388§	0.293

* Untreated original.

† Aged seven days at 130°C.

‡ Evacuated at 3×10^{-4} mm.; aged seven days at 130°C.

§ One hundred and nineteen days.

TABLE 6

Results obtained with preheated ethyl phthalate as solvent

SPECIMEN	VISCOSITY SLOPES					
	24 hours	7 days	14 days	42 days	84 days	168 days
E. K., untreated	1.664		0.938	0.853	0.507	0.319
E. K., aged*	1.776		1.072	0.778	0.594	0.406
E. K., evacuated, aged	1.81		1.091	0.724	0.571	0.393
E. K.,† evacuated, aged	1.759		0.988	0.736	0.621	0.349
N, untreated	1.637		1.242	0.926	0.703	
N, evacuated, aged	1.750		1.16	0.87	0.66	
E. K. (July, 1927), untreated	1.786	1.347	1.49			
E. K. (July, 1927), evacuated, aged	1.800	1.42	1.298			

* In all cases aging was for seven days at 130°C.

† *Trace of nitrocotton added; slight apparent decomposition.*

In contrast to experiments on previous heating of the solvent alone were the experiments previously reported (reference 6, table IV, p. 320) on heating the dry nitrocotton at 60°C. Subsequent experiments, but heating in sealed tubes evacuated to 0.0002 mm., have shown that samples are somewhat erratic, some being only slightly yellow after six months at 60°C. in an evacuated tube, whilst others were brown or reduced to a moist black mass. Where brown fumes appeared after a week, they disappeared again. It was found that the viscosity of solutions in ethyl formanilide, when the nitrocotton had previously been heated for 84 days at 60°C., was only one-eighth of its usual value. These experiments disprove the alternative hypothesis suggested by others that the degradation consists in oxidation of the nitrocotton by the air.

PROLONGED AGING OF SOLUTIONS

In the previous communication[8] it was shown that when solutions of nitrocotton are made up and kept in the dark at 55°C., their viscosity falls approximately with the logarithm of the time over periods of six months to a year. Reasons were given for believing that this was due to degradation or to a physical dismemberment of the cellulose aggregates rather than to denitration of the nitrocotton or nitration of the solvent. These tubes have been kept under observation for further periods up to as much as three years.

In several cases a noteworthy new phenomenon has been observed. Several of these solutions which had been steadily losing their viscosity began to set to jellies. For example, the benzylformanilide solutions (sample 1/10/20, reference 6, p. 333) jellied between the ages 200 to 300 days. These jellies were broken up by shaking at 55°C., but again set to jellies within a few more hours at 55°C. The similar solutions in a later purer sample (16/2/25, reference 6, p. 333) were still fluid at 770 days. Similarly, solutions in ethylformanilide (reference 6, p. 330) began to jelly after 700 days at 55°C. Finally, the solutions in ethyl phthalate (Nobel's; December, 1923; reference 6, p. 330) began to increase in viscosity towards the end of three years. Here again an explanation of these enormous viscosity changes in both directions is not to be sought in a change in the length of the molecule itself. It bears rather the hall-marks of structural viscosity.

The data for these very long periods are given in condensed summary in table 7, the values at 24 hours being included for comparison. The designations of some of the solvents refer to the previous communication. In scrutinizing the data it should be remembered that the viscosity slopes will

[8] Pp. 329-44, especially table XI and figures 5 and 6. Reference should be made to the standard work of Sir Robert Robertson on the slow decomposition of nitrocellulose at 135°C. (ROBERTSON, R., AND NAPPER, S. S.: J. Chem. Soc. 91, 764 (1907)).

TABLE 7

Viscosities of solutions of nitrocotton kept at 55°C. for prolonged periods (measurements by L. E. S. and E. M. G.)

SOLVENT	VISCOSITY SLOPES					
Benzylphenylurethan (March 13, 1924)	Days	1	329	700	986	
	Slope	1.995	0.288	0.219	0.158	
Ethyl phthalate* (Nobel's; December, 1923)	Days	1	326	697	978	
	Slope	2.05	0.55	0.101	0.163	
Ethyl phthalate* (Eastman Kodak)	Days	1	324	661	937	
	Slope	1.97	0.232	0.107	0.112	
Ethylformanilide (May, 1924)	Days	1	328	694	(800)	
	Slope	0.872	0.085	0.047	Jellying	
Ethylphenylurethan (March, 1923)	Days	1	327	690	980	
	Slope	1.80	0.286	0.095	0.048	
Methylphenylurethan (August 8, 1923)	Days	1	326	688	968	
	Slope	1.605	0.246	0.230	0.0748	
Formanilide (Nobel's; May, 1924)	Days	1	328	681		
	Slope	1.02	0.034	0.029		
o-Tolylurethan (April 15, 1924)	Days	1	328	666	941	
	Slope	1.715	0.268	0.107	0.051	
Phenylurethan (August, 1923)	Days	1	330	674	930	
	Slope	1.435	0.115	0.074	0.034	
Phenylurethan† (Nobel's; July, 1925)	Days	1	14	384		
	Slope	1.365	0.78	0.154		
Benzophenone (November, 1923)	Days	1	330	672		
	Slope	1.58	0.277	0.136		
Benzophenone (Kahlbaum)	Days	1	14	138	506	786
	Slope	2.04	1.39	0.915	0.306	0.217
Benzophenone (Nobel's; April 2, 1925)	Days	1	14	139	505	786
	Slope	1.76	1.34	0.94	0.284	0.159

* Particles of nitrocotton separate from the ethyl phthalate solutions after long periods of aging. Some evidence of a similar behavior was noted with acetone.

† Specially purified. Similarly purified formanilide (N) did not dissolve quite all the nitrocotton fibers. The true slope must therefore exceed the observed value, 0.80.

TABLE 7—*Concluded*

SOLVENT	VISCOSITY SLOPES					
Benzophenone† (M)	Days	1	14	387	668	
	Slope	1.56	1.12	0.291	0.196	
Benzylformanilide (February 16, 1925)	Days	1	84	203	572	769
	Slope	1.23	0.345	0.161	0.068	0.053
Diethyl carbonate (N)	Days	1	14	18	373	
	Slope	1.585	0.86	0.69	0.26	
Diacetone alcohol (N)	Days	1	15	19	371	
	Slope	0.82	0.45	0.49	‡	
Ethyl acetoacetate (N)	Days	1	14	367		
	Slope	0.91	0.565	0.055		
Ethyl lactate (N)	Days	1	14	365		
	Slope	1.080	0.830	0.269		
Ethyl benzoate (N)	Days	1	14	363		
	Slope	1.49	1.014	0.283		
Ethyl oxalate (N)	Days	1	348			
	Slope	1.56	0.48			

‡ A 0.4 and a 0.5 per cent nitrocotton solution now exhibit a viscosity 0.00927 and 0.00940, respectively, as compared with the original solvent itself, 0.01383, presumably owing to progressive condensation of the solvent.

become zero when the viscosity of the solutions has fallen to that of the solvent. In no case is this attained or attainable even if only the lowest possible degradation products were left in solution. The lowest final slope is 0.03, where the viscosity is only 3 per cent higher than that of the solvent itself. The initial (logarithmic) slopes were several fold or many fold that of the solvent even for these very dilute (0.35–0.4 per cent) solutions.

The last six more mobile solvents of table 7 were all measured (L. E. S.) subsequent to the previous publication.

SOME DATA FOR ANOTHER SIMILAR NITROCOTTON

Five-tenths per cent solutions were prepared and measured in the usual way at 55°C., using the 1919 and a 1927 sample[9] of nitrocotton with the results given in table 8. The behavior is parallel, and furfural appears as an excellent solvent.

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[9] Nitrogen, 12.24 per cent; nitrogen (ash-free), 12.26 per cent; ash, 0.13 per cent; solubility in ether-alcohol, 99.4 per cent.

At room temperature a 7 per cent solution in furfural is almost too viscous to flow. Two solutions of the 1927 sample in amyl acetate (B. D. H) prepared at 55°C. and measured at 25°C. at 1 day contained 2.102 per cent and 4.618 per cent, respectively. Their densities were 0.8685 and 0.8888 and their viscosities 8.828 and 19.49 (falling ball method), giving viscosity slopes 7.57 and 9.52.

TABLE 8

Comparison of viscosities of 1919 and 1927 nitrocotton solutions at 55.00°C.

SOLVENT	NITRO-COTTON	VISCOSITY SLOPES				
		1 day	7 days	14 days	42 days	84 days
Ethylphenylurethan (N; November, 1926)	1919	1.472		1.002	0.583	0.312
	1927	2.184		1.405	0.744	0.396
Methylphenylurethan (N; November, 1926)	1919	1.470		0.984	0.727	0.514
	1927	2.243		1.577	0.968	0.467
Phenylurethan (N; May, 1925)	1919	1.433		0.881		
	1927	2.294		1.007		
Phenylurethan* (N; July, 1925)	1927	2.481			0.392	0.217
Furfural (B. D. H.)	1919	1.383				
	1927	1.971	1.829	1.745		

* Specially pure.

DISCUSSION

It is amply established that the viscosity of a solution of nitrocotton in a definite solvent at a definite temperature depends upon a large number of other factors such as previous mechanical treatment, slight impurities, etc. A large part of this behavior must be ascribed to structural viscosity in accordance with the general hypothesis advanced by one of us on a previous occasion (4). It is obviously not to be explained as being due to alterations or fluctuations in the length or size of the cellulose molecule itself.

In general, the solvent power of various solvents may be defined as following the indications of the viscosity slopes; the lower the (relative) viscosity, or rather, viscosity slope, the better the solvent. Thus it would appear from the new data here presented that diacetone alcohol, ethyl acetoacetate, and ethyl lactate[10] are excellent solvents, and that ethyl benzoate and ethyl oxalate are good solvents for this type of nitrocotton.

Degree of solvent power is necessarily inferred from indirect methods, since true solubility in the usual sense is not present. Such indirect methods are the determination of the percentage of nitrocotton dissolved under specified conditions (1), the position of minimum viscosity in mix-

[10] The slope for ethyl lactate (N) at 55°C. and 1 day was 0.86, and after drying was 0.80.

tures (3) (found to dissolve cellulose derivatives most readily), the determination of the amount of a diluent which the solvent can bear (2), and the minimum temperature at which the solvent dissolves the cellulose derivative (2). Others will now be briefly described.

It is a serious complication that in mixtures a liquid chosen as diluent may actually reinforce and improve the solvent power, as in the well-known case of alcohol and ether or of toluene and alcohol for nitrocotton of low nitrogen content (8). The nearest approach to a perfect diluent or a non-solvent is a low-boiling, saturated paraffin[11] such as hexane.

Further methods tried by one of us (L. E. S.) and found promising are as follows:

1. Adding to a diluent a solvent until the nitrocotton is just gelatinized (compare p. 1221). End points are more indefinite with alcohol and chloroform as diluents than with benzene. The addition of only a few per cent of a good solvent converts ethyl alcohol into a solvent. Many times larger amounts are required for chloroform and benzene, but the order of the solvents is not the same in the three cases. Of five tested, acetone and ethylformanilide were most effective with chloroform and benzene, and nitrobenzene least so. Ethylphenylurethan was next best, but excelled with alcohol. This method is less sharp than that of precipitating with diluents, but the results are parallel with those obtained by viscosity measurements.
2. A rapid approximate method is to pour dilute solutions of solvents in hexane upon nitrocotton and to note the very different swelling, greatest for ethylformanilide and least for benzylphenylurethan.
3. The sorption of solvents from solution in hexane by means of nitrocotton may be measured by noting the refractive index of the supernatant liquid by a differential method. Nitrocotton sorbed ethylformanilide most, to an extent exceeding its own weight, but ethylphenylurethan and benzylphenylurethan far less.
4. Finally, if 1 g. of nitrocotton is added to about 15 g. of various liquids, the temperature is raised by about 0.1°C. by non-solvents and by several degrees by good solvents. Others may give intermediate values, and the results are easily distorted if very volatile solvents are employed.

All the varied methods of testing solvent power give in general more or less comparable results. Precise comparison and classification are affected by the very numerous factors involved and the specific properties of the sample of cellulose derivative under test.

Hutchinson compared the times required under comparable conditions for nine solvents just to dissolve 0.5 per cent of nitrocotton. Of these ethyl lactate was by far the quickest, requiring only three-quarters of an hour

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[11] E. W. J. Mardles (J. Soc. Chem. Ind. 42, 132T (1923)) used petroleum spirit (b.p. 90-100°C.).

with slow rocking at 55°C. Taking this time as unity, the other solvents were as follows: ethylformanilide, 5; formanilide, 16; ethyl phthalate, 21; benzylformanilide, 24; ethylphenylurethan, 28; *o*-tolylurethan, 49; benzophenone, 56; benzylphenylurethan, 80. The exact order appears to be of little significance and only very roughly does it parallel the viscosity slopes either immediately after solution or after 14 days or in standard experiments at 24 hours or 14 days at 55°C., ethyl phthalate being a prominent exception.

It should be placed upon record that particles seen in solutions of nitrocotton in ethylformanilide or ethylphenylurethan, when examined even under Zsigmondy's immersion Winkel ultramicroscope, are so few in number that it is certain that the greater part of the nitrocotton is invisible in the highest powers of the ultramicroscope.

The rule that the viscosity slope falls off towards zero in approximate proportion to the logarithm of the time as if the structural viscosity would have disappeared in one or two years appears to be of fairly general application. As would be expected from the hypothesis of dismemberment of nitrocotton micellar aggregates by the solvent, it is independent of the concentration, as was shown by Hutchinson with concentrated solutions in diethyl carbonate and in ethyl lactate; namely, 2.675 per cent and 3.141 per cent nitrocotton, respectively. When first measurable, their viscosities were 42.9 poises at 3 days for the diethyl carbonate solution and for the ethyl lactate 28.9 poises at 3 hours, falling to 6.17 poises at 5 days. Both quickness of dissolving and comparatively low viscosity slope indicate ethyl lactate to be much superior to diethyl carbonate as a solvent. Another 2.3 per cent solution in diethyl carbonate lost in 14 days 92 per cent of the viscosity possessed immediately upon solution. Films made from concentrated solutions in ethyl lactate dried very slowly, whilst those from amyl acetate and diethyl carbonate exhibited tensile strengths (W. B. Lee) of between 8000 and 11,000 lbs. per square inch. Further examination is required to test the effect of time and the possible influence of a skin formation.

SUMMARY

1. Experiments are described with over one hundred solvents and solvent mixtures, some of very high purity. The results confirm and extend our previous findings. They emphasize that the chief factor involved in the apparent or effective viscosity of nitrocotton solutions is structural viscosity due to colloidal aggregates of easily varied degree of ramification and dismemberment.

2. The time experiments at 55°C. were extended to three years, when some of the solutions are approaching the viscosity of the pure solvent within a few per cent, an enormous drop in viscosity. However, in several

cases, the viscosity passes through a low minimum and the solutions may afterwards even set to jellies.

3. Four other new methods of determining degree of solvent power are very briefly indicated.

We have great pleasure in acknowledging the invaluable support and coöperation of Messrs. Nobel's Explosives Co., Ltd., and the unfailing interest of their scientific staff, which have rendered this work possible.

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NEW BOOKS

Conductometric Analysis. By H. T. S. Britton. 14 x 21 cm.; ix + 178 pp. London: Chapman and Hall, Ltd., 1934. Price: 12s. 6d.

Although the suggestion that analytical titrations could be followed by measurement of conductivity was made by Kohlrausch as long ago as 1885, the possibilities of the method did not receive the attention paid to the potentiometric method of titration. The chief reason for this neglect was probably the fact that the accurate measurement of conductivity has been a matter of some difficulty. In recent years, however, as a result of developments in connection with the use of the thermionic valve and of the introduction of other means of producing and rectifying alternating currents, the procedure has been very much simplified, so that the potentialities of the method are being more fully studied. The only collected work on conductometric analysis has hitherto been the excellent monograph *Konduktometrische Titrationen* by Kolthoff, and so the book under review will be welcomed by those who prefer their scientific literature in the English language.

The first two chapters deal with the general theoretical aspects of electrical conductivity; they are followed by two further chapters on conductivity titration apparatus and methods. Although the various principles involved in the measurement of conductivity are adequately discussed, it is strange that no details are given of the actual method of *titration*, since it is essentially different from that used in ordinary volumetric or potentiometric analysis. Sections on the titration of strong and weak acids and bases of various kinds are followed by a discussion of replacement and precipitation reactions, and of the use of mercuric perchlorate as a titrant. The next three chapters deal with abnormal acids, the precipitation of metallic bases and the application of conductometric titration to research; they are more particularly concerned with the author's own work and are of somewhat specialized interest. The book concludes with an interesting, although perhaps too concise, description of industrial applications which serves to show the scope of the conductometric method of analysis.

It is a matter of regret that the author frequently uses the Arrhenius theory of ionization as a basis of his discussion, so that the language is often obsolete and misleading from the modern standpoint; the main principles underlying conductometric titrations are, however, treated quite adequately. The book is well produced and contains a commendable number of clear diagrams which add considerably to its value.

S. Glasstone.

Molekülstruktur. By H. A. Stuart. 22 x 14 cm.; x + 388 pp. Berlin: Julius Springer, 1934. Price: paper, 32 RM; bound, 33.80 RM.

The rapid advances made in recent years in the determination of the shapes and sizes of molecules by modern physical and physicochemical methods have led to a desire on the part of many chemists for a concise and intelligible summary of the results. This is provided very well in Dr. Stuart's book, which is characterized by a satisfactory, though brief, exposition of experimental methods, and the absence of difficult mathematics. These features, together with the numerous tables of numerical results and copious references to the literature, combine to produce a work of special appeal and service to chemists working in other fields who wish to acquaint themselves with the procedure and data of the new methods. The topics dealt with include the theories of valence and molecular forces, nuclear distances and configurations, electric moment, Raman effect, Kerr effect, electron diffraction, infra-red spectra, proper vibrations, valence angles, potential curves, and dissociation. The treatment, although necessarily brief, is quite sufficient to bring out the main features of the methods, and although many important matters are dealt with in a small space, it cannot be said that the book is in any way superficial. In some cases the treatment lacks completeness, e.g., in the discussion on specific heats of gases no high temperature methods or results are included, and the picture is too much idealized, but on the whole a very fair balance of treatment is preserved, and the indexes are good. The volume is one which can be warmly recommended. It satisfies a definite need in chemical literature.

J. R. PARTINGTON.

Chemie der Enzyme, Pt. 2, Section 3. By HANS V. EULER. 26 x 17 cm.; xi+ 663 pp. München: J. F. Bergmann, 1934. Price: 58 RM.

In this volume, Prof. Hans V. Euler and his colleagues, Franke, Nilsson, and Zeile, cover the chemistry of catalase and the enzymes concerned in oxidation and reduction. The section on fermentation remains to be published. It is almost unnecessary to inform readers of the former volumes that every serious student of enzyme chemistry will find this book essential.

While the action of hydrolytic enzymes can be studied individually *in vitro*, most biological oxidations are complex processes involving several catalysts, and their analysis is often very incomplete. Hence, the physical chemist will find pp. 76–364, which deal with the general process of respiration, rather heavy going, in spite of their excellent summary of Warburg's photochemical investigations. On the other hand, the accounts of the individual enzymes, e.g., catalase, peroxidase, and succinodehydrase, which can be studied separately, are of wider interest. Inhibition by excess of substrate is particularly characteristic of these enzymes, which may have optimum substrate concentration below 10^{-4} *M*.

Physical chemists will be interested in the discussion of Willstätter and Haber's chain reaction theory. On the other hand, they may feel that oxidation-reduction potentials might have received rather more attention.

It is perhaps inevitable that some aspects of enzyme chemistry, e.g., Moelwyn-Hughes' theory of activation, should not be touched on in this volume. We may hope for a new edition, within a few years, of the first volume of this book, in which such general problems are treated. On the other hand, students of non-biological oxidations at low temperatures will find numerous references to non-enzymatic catalysis, e.g., the oxidation of sugars in presence of heavy metal salts, that of ammo-acids in presence of charcoal and of synthetic haemochromogens, which have appeared in biological journals little read by most chemists.

While, therefore, this book is indispensable to the biochemist, the physical chemist will find that it contains valuable information on many aspects of catalysis.

J. B. S. HALDANE.

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