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THE TERNARY SYSTEM, K_2SiO_3-Na_2SiO_3-SiO_2

BY F. C. KRACEK

The equilibrium phase relations in the ternary system of silica with the two important alkali oxides, Na_2O and K_2O, have not been previously subjected to a systematic study. The knowledge of the phase relations in this system has a bearing on petrology, since the two alkali oxides, Na_2O and K_2O, are important constituents of the common silicate minerals occurring in rocks; the system is also of some interest in glass technology, the three components of the system entering in varying amounts into the composition of commercial glasses. From another point of view the phase relations in this system are of theoretical interest especially in that the results of the present work establish a unique type of solid solution sequence between the two disilicates, $K_2Si_2O_5$ and $Na_2Si_2O_5$.

The component-binary systems, K_2SiO_3-SiO_2 and Na_2SiO_3-SiO_2, have already been published from this Laboratory.[1,2,3] The information given in the papers quoted must be considered together with the additional data published in this paper in arriving at the correct representation of the phase relations in the ternary system.

The reader is referred to previous papers from this Laboratory for descriptions of the methods, apparatus, and technic employed in the somewhat specialized field of silicate research. No attempt is made in this paper to describe the experimental technic in more detail than is needed to make each point at issue clear.

Preparation of Materials

The mixtures studied were prepared in the form of glasses from Na_2CO_3, K_2CO_3 and quartz. The Na_2CO_3 used was obtained by dehydration of exceptionally pure $Na_2CO_3.H_2O$. The K_2CO_3 was derived from $KHCO_3$, also of high purity. The quartz was taken from the special stock of this Laboratory, containing certainly less than 0.05 per cent impurities.

The compositions were made up by heating mixtures of weighed amounts of the reagents, according to a definite procedure. Platinum crucibles were used throughout. Experience has shown that the best results are obtained when the mixed reagents are allowed to sinter slowly at as low a temperature as possible for the reaction to proceed, usually not above 700°C. Most of the CO_2 is driven off quietly when this is done, and mechanical losses due to bubbling or spattering are completely eliminated. When a large number of mixtures is being prepared, it is best to conduct the sintering in individual, controlled furnaces, allowing about 24 hours for the process. The crucible and

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[1] Kracek, Bowen, and Morey: J. Phys. Chem., 33, 1857 (1929).
[2] F. C. Kracek: J. Phys. Chem., 34, 1583 (1930).
[3] Morey and Bowen: J. Phys. Chem., 28, 1167 (1924).

contents are then weighed to estimate the amount of CO_2 still undisplaced. About 99 per cent of the total CO_2 should be expelled before proceeding to the next stage of the heating. The temperature is now raised slowly to drive off the rest of the CO_2. There should be no frothing of the melted glass, otherwise mechanical losses are unavoidable. In addition to the mechanical losses, there may be losses occasioned by the vaporization of the undissociated carbonates with the escaping CO_2. After the CO_2 is displaced, the temperature may be raised to 1200°C or higher for a brief period to facilitate diffusion in the molten mixture. It is essential to note that CO_2-free mixtures lose very little Na_2O or K_2O by volatilization even at moderately high temperatures.

After the first melting the glass is crushed, thoroughly mixed, and replaced in the furnace for a second melting. The process is repeated until no inhomogeneity can be detected in the glass when examined under the microscope, using an immersion liquid matching it in refractive index.

Control of the Composition of the Preparations

During the preparation of the mixtures record is kept of the weights at each stage of the process. It is assumed here that no SiO_2 is volatilized. Kracek showed[2] that the volatility of Na_2O from Na_2O-SiO_2 mixtures containing more than 60 per cent SiO_2 is negligible when an exact procedure is being followed. The volatilization losses in the preparation of the K_2O-Na_2O-SiO_2 mixtures in the present work were generally of the order of 0.1 to 0.3 per cent, and the assumption is being made that the losses were due solely to the volatilization of K_2O.

A number of the synthetic compositions were checked by direct analysis. Owing to the difficulties inherent in the separate determination of sodium and potassium when both are present in the same sample, the Na/K ratio can be determined with only moderate precision. It was found that the compositions as established by synthesis were correct to within the uncertainty of the analyses, which was of the order of 0.5 per cent on duplicate samples.

The compositions given in the tables are for this reason the synthetic compositions in all cases. This procedure is assumed to be justified further by the general concordance of all the results leading to the derivation of the liquidus surfaces presented in Figs. 1 and 2. The assumption made, that all the volatilization losses are due to K_2O, is definite, and the systematic errors thus introduced into the diagram are well within the experimental error of the analytical determination; they are of major importance only in the sense that a slight distortion of the fields in the region of equimolar Na/K ratio may be produced. For example, let us assume that as much as 0.5 per cent volatilization loss is encountered with a hypothetical synthetic mixture represented by 25 per cent K_2O, 25 per cent Na_2O, and 50 per cent SiO_2. If we assume that K_2O and Na_2O have equal volatilities the composition of the mixture would be 25.25 per cent K_2O, 24.75 per cent Na_2O, and 50 per cent SiO_2. The actual composition of the mixture would certainly lie between the two limits, and most probably nearer the 25:25:50 ratio, since K_2O is distinctly more volatile than Na_2O. Analysis can not decide between these possibilities; it is hence assumed, barring large accidental errors, that the compositions given in the tables are correct to within a maximum *systematic* error of 0.3 per cent.

Liquidus Determination

The "quenching" method of liquidus determination, generally employed in silicate work in this Laboratory, has been used with all the preparations studied in this investigation.

The individual preparations were first crystallized by appropriate heat treatments; the crystal aggregate was then powdered and well mixed to further insure good homogeneity of the preparation, and was then used in the quenching work to determine the liquidus. The quenching furnace control was thermostatic to within 0.5°C. The temperatures were read by calibrated Pt vs. Pt-Rh (10% Rh) thermocouples in connection with the temperature scale of this Laboratory.[4] A Wolff-Feussner potentiometer with a highly sensitive galvanometer was used in the temperature measurements, all necessary precautions being observed.

Compositions in the K_2SiO_3 and Na_2SiO_3 fields crystallize readily. In the disilicate fields, *i.e.*, $K_2Si_2O_5$ and $Na_2Si_2O_5$, a variety of behavior is encountered. In general, those preparations whose compositions contain more K_2O or Na_2O than is required to yield a disilicate can be crystallized with ease in the dry state. Preparations with more SiO_2 than is required for a disilicate can usually be crystallized in the dry way only if the liquidus lies above 750°, or if they lie near the disilicate join. When a much larger excess of SiO_2 is present, crystals will not grow even in seeded preparations in the dry state if the liquidus is much below 750°, and hydrothermal crystallization must be employed.[1,5,6] Similar considerations apply to the fields of $K_2Si_4O_9$ and of quartz. Tridymite can usually be crystallized from the mixtures in which it forms the stable phase, without any particular difficulty, in the dry way, if sufficient time is allowed; it is to be noted, however, that there is a preponderant tendency for cristobalite to be formed at first, and sufficient time must be given in the initial crystallization to convert the (metastable) cristobalite to tridymite.

Since diffusion in the more or less viscous vitreous melts is not very rapid, enough time must be given each preparation in the melting point experiments to come to equilibrium before quenching. One hour or less suffices for the attainment of equilibrium at or near the liquidus temperature in the K_2SiO_3, Na_2SiO_3, and certain portions of the $K_2Si_2O_5$ and $Na_2Si_2O_5$ fields. In general when the SiO_2 content lies between 60 and 75 wt. per cent, very much greater length of time must be allowed for the attainment of equilibrium, the time required increasing inversely with the liquidus temperature. When the

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[4] Intern. Crit. Tables, 1, 57; Day, Sosman, and Allen; Carnegie Inst. of Washington, Publ. 157.

[5] Morey and Fenner: J. Am. Chem. Soc., 39, 1173 (1917).

[6] Morey, Kracek, and Bowen: J. Soc. Glass Tech., 14, 149 (1930).

liquidus temperature lies below 700°C at least 6 to 12 hours must be allowed; in the quartz field a time of 48 hours or more often fails to dissolve the larger grains. Tridymite dissolves more promptly, and usually 2 to 5 hours are sufficient to reach equilibrium.

It is obvious that dynamic methods of liquidus determination are not applicable to materials of this type. The "quenching" method,[7] more accurately described as a static equilibrium method, when applicable, can give information not only about the liquidus or other transformation temperatures, but also with regard to the nature of the phases present at equilibrium. The principal requirement of the method is that nucleation of new crystals should be sufficiently slow so that the sample can be chilled to room temperature (by quenching in a non-reacting liquid when necessary) while retaining the structure reached during the thermostatic heating at the desired temperature. The sample is then examined under the microscope to determine whether crystals are present, and their character. By varying the temperature, the limits between which the sample exhibits one phase or another can be fixed as closely as desired. The great advantage of the method lies in the fact that the thermostatic heating at each temperature can be prolonged until equilibrium is attained in the sample.

The Experimental Results

It has been customary to present the results of phase rule studies on silicates from this Laboratory in the form of a more or less abbreviated record of the actual quenching experiments performed.

In view of the large number of preparations studied in this work, and the relative simplicity of the system (there being no ternary compounds), it is deemed advisable here to present the results in a briefer form. The tables following present the synthetic compositions of the mixtures, the equilibrium transformation temperatures, and the temperature interval within which the transformation temperature is located. Thus, if the liquidus temperature is given as 764°, interval $+3-2$, it is meant that the preparation when quenched from 767° was all glass, and when quenched from 762° it contained crystals. Since the thermostatic control of the furnace is accurate to 0.5°, the limits 767° and 762° are intended to denote that these temperatures are known to the nearest 0.5° of the values given; the interval then denotes the limits within which the transformation was determined, and not the uncertainty of the temperature measurement.

The data are given in Table I. In constructing the ternary diagrams, Figs. 1 and 2, use was made of the already mentioned results on the component-binary systems, K_2SiO_3-SiO_2 and Na_2SiO_3-SiO_2,[1,2] together with the work of Kracek on the cristobalite liquidus.[8]

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[7] Originally described by Shepherd and Rankin: Am. J. Sci., 28, 308 (1909).

[8] F. C. Kracek: J. Am. Chem. Soc., 52, 1436 (1930).

TABLE I

Compositions and Liquidus Temperatures of Preparations studied Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K_2O	Na_2O	SiO_2				
A. Solid Phase: Na_2SiO_3							
574	—	50.82	49.18	1089	+0.5-0.5	1	CG
2	10.7	41.5	47.8	1009	+4-4	1	C
3	17.7	36.2	46.1	963	+3-3	1	C
4	24.6	31.3	44.1	912	+3-3	3	G
5	32.0	24.5	43.5	858	+4-4	2	G
6	39.1	18.7	42.2	842	+4-4	2	G
7	42.3	15.8	41.9	759	+4-4	3	G
8	38.6	16.7	44.7	780	+5-5	3	G
9	34.9	17.5	47.6	754	+2-2	2	G
10	37.1	13.9	49.0	682	+4-4	3	C
11	26.9	19.4	53.7	729	+2-2	2	CG
12	25.0	17.7	57.3	672	+4-4	3	CG
13	22.3	23.2	54.5	788	+3-3	2	G
14	20.1	20.9	59.0	689	+4-4	4	C
15	14.6	29.4	56.0	847	+4-4	3	C
16	13.1	26.9	59.9	765	+3-3	2	C
17	8.0	31.3	60.7	796	+3-3	2	C
B. Solid Phase: $Na_2Si_2O_5$							
21	—	34.05	65.95	875	+0.5-0.5	2	C
22	3.8	31.1	65.1	827	+2-2	2	C
23	7.2	28.6	64.2	789	+3-3	2	C
24	9.5	26.8	63.7	758	+1-2	2	C
25	12.1	24.8	63.1	739	+3-3	2	C
26	15.8	21.9	62.3	730	+2-2	4	C
27	18.8	19.7	61.6	723	+1-1	12	C
28	22.8	16.5	60.7	711	+3-3	12	C
29	23.9	17.1	59.0	695	+2-2	12	C
30	12.5	25.9	61.6	729	+1-1	12	C
31	7.8	29.9	62.3	776	+2-2	3	C
32	7.0	27.2	65.8	792	+2-2	6	C
33	6.6	25.8	67.6	787	+1-1	6	C
34	6.2	24.5	69.3	780	+1-1	8	C
35	3.7	26.4	69.9	808	+2-2	6	C
36	5.8	22.7	71.5	755	+1-1	10	C
37	11.2	23.0	65.8	753	+1-1	8	C
38	10.5	21.4	68.1	751	+1-1	12	C

* The symbols G, C, B denote that the material used for the quenching experiments was G glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE I (Continued)

Compositions and Liquidus Temperatures of Preparations studied Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K_2O	Na_2O	SiO_2				
39	9.8	20.1	70.2	735	+2−2	10	C
40	14.1	18.5	67.4	726	+2−2	8	C
41	21.5	15.2	63.3	707	+2−2	8	C
42	19.9	14.2	65.9	679	+4−4	16	B
43	18.9	13.3	67.8	649	+2−2	8	B
44	18.2	13.1	69.7	638	+2−2	24	B
45	21.6	9.6	68.8	597	+3−3	24	B
115	9.1	18.9	72.0	723 m	+3−3	6	C
117	5.3	21.7	73.0	741 m	+3−3	6	C
			C. Solid Phase: K_2SiO_3				
M	(61.1)	—	(38.9)	976	—	—	—
51	50.6	8.7	40.7	902	+3−3	0.5	CG
52	47.3	12.1	40.6	833	+4−4	1	CG
53	41.7	11.1	47.2	702	+2−2	2	CG
			D. Solid Phase: $K_2Si_2O_5$				
251	43.8	—	56.2	1036	+1−1	1	CG
61	42.3	1.4	56.3	1008	+1−2	1	CG
62	38.4	4.5	57.2	954	+2−3	2	CG
63	36.8	5.5	57.7	924	+2−2	2	CG
64	34.6	7.6	57.8	898	+2−2	2	CG
65	32.9	8.6	58.5	878	+2−2	3	CG
66	30.2	10.9	58.9	831	+1−1	3	C
67	27.0	13.2	59.8	765	+1−1	12	C
68	40.9	1.3	57.8	1000	+1−1	1	CG
69	38.9	1.3	59.8	978	+1−2	1	CG
70	36.9	1.2	61.9	973	+2−2	2	CG
71	35.8	1.2	63.0	951	+2−2	2	CG
72	34.6	1.2	64.2	925	+2−3	2	CG
73	33.9	1.1	65.0	890	+2−2	2	CG
74	32.8	1.1	66.1	861	+3−3	3	C
75	31.9	1.1	67.0	826	+3−3	3	C
76	35.6	4.2	60.2	928	+2−2	3	CG
77	33.6	4.0	62.4	883	+2−3	8	C
78	29.9	3.6	66.4	798	+2−2	12	C
79	31.2	8.0	60.8	860	+5−5	6	C
80	28.9	7.5	63.6	807	+4−4	4	C
81	27.3	7.1	65.6	750	+5−5	6	B

* The symbols G, C, B denote that the material used for the quenching experiments was G glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE I (Continued)

Compositions and Liquidus Temperatures of Preparations studied Quenching Method

Preparation number	Composition in weight per cent			Liquidus temp. °C	Determined interval °C (see p. 2532)	Time allowed to reach equilibrium (hours)	Initial condition*
	K_2O	Na_2O	SiO_2				
82	25.7	6.6	67.7	667	+2-2	24	B
83	24.7	11.7	63.6	698	+4-4	6	B
84	44.8	1.5	53.7	1002	+2-2	1	CG
85	47.3	1.5	51.2	975	+2-2	1	CG
86	48.4	1.6	50.0	935	+2-3	1	CG
87	49.8	1.6	48.6	865	+5-5	1	CG
88	50.7	1.7	47.6	816	+4-4	1	CG
89	51.6	1.7	46.7	789	+4-4	1	CG
90	46.9	3.7	49.4	860	+5-5	1	CG
91	40.9	4.9	54.2	948	+3-3	1	CG
92	45.0	5.3	49.7	843	+3-3	1	CG
93	35.6	9.3	55.1	864	+4-4	1	CG
94	39.2	10.0	50.8	785	+5-5	1	CG
95	40.5	10.8	48.8	693	+3-3	1	CG
96	34.7	13.1	52.2	730	+5-5	1	CG
97	31.9	15.5	52.5	715	+5-5	1	CG
E. Solid Phase: $K_2Si_4O_9$							
284	28.1	—	71.9	765	+0.5-0.5	24	B
101	26.9	3.2	69.9	700	+2-2	24	B
F. Solid Phase: Quartz							
110	24.5	2.9	72.6	798	+4-4	48	B
111	23.4	6.0	70.6	700	+10-10	75	B
112	20.9	5.5	73.6	810	+5-5	24	B
113	16.0	11.3	72.7	783	+4-4	24	B
114	13.3	15.7	71.0	688	+4-4	50	B
115	9.1	18.9	72.0	750	+5-5	24	B
116	8.2	16.9	75.0	865	+5-5	30	B
117	5.3	21.7	73.0	786	+3-3	30	B
G. Solid Phase: Tridymite							
121	22.4	2.6	75.0	902	+3-3	6	C
122	20.9	2.6	76.5	976	+4-4	4	C
123	16.9	2.8	80.3	1168	+4-4	2	C
124	17.9	4.6	77.5	1035	+5-5	4	C
125	14.3	10.2	75.5	905	+5-5	5	C
126	10.5	7.4	82.1	1235	+5-5	3	C
127	7.2	15.4	77.4	980	+5-5	5	C
128	4.0	11.7	84.3	1310	+5-5	3	C

* The symbols G, C, B denote that the material used for the quenching experiments was glassy, C crystallized dry, or B crystallized hydrothermally in bombs. CG denotes that liquidus was determined starting with both glassy and pre-crystallized materials.

TABLE II
Invariant Points*

	Type	Crystal phases in coexistence with liquid	t°C	Composition of liquid weight per cent		
				K_2O	Na_2O	SiO_2
E_1	Ternary eutectic	K_2SiO_3, Na_2SiO_3, $K_2Si_2O_5$ I	645	40.1	11.7	48.2
E_2	”	$K_2Si_2O_5$ I, Na_2SiO_3, $Na_2Si_2O_5$ II	665	25.4	17.2	57.4
E_3	”	$K_2Si_2O_5$ II, $Na_2Si_2O_5$ II, Quartz II	540	23	8	69
E_4	Binary eutectic	K_2SiO_3, $K_2Si_2O_5$ I	775	54.5	—	45.5
E_5	”	$K_2Si_2O_5$ I, $K_2Si_4O_9$ I	752	31.0	—	69.0
E_6	”	$K_2Si_4O_9$ I, Quartz I	764	27.6	—	72.4
E_7	”	Na_2SiO_3, $Na_2Si_2O_5$ I	846	—	37.9	62.1
E_8	”	$Na_2Si_2O_5$ I, Quartz I	793	—	26.1	73.9
E_9	”	Na_2SiO_3, K_2SiO_3	745	43	15	42
E_{10}	”	$Na_2Si_2O_5$ I, $K_2Si_2O_5$ I	705	24.5	15.0	60.5
A	Unmixing	$K_2Si_2O_5$ I and mixed crystals	814	52.5	—	47.5
B	”	$K_2Si_2O_5$ I and mixed crystals	993	40.4	—	59.6
C	”	Na_2SiO_3, $Na_2Si_2O_5$ I and mixed crystals	740	11.5	27.0	61.5
D	”	Quartz I, $Na_2Si_2O_5$ I and mixed crystals	765	4.0	23.5	72.5
F	Inversion	$K_2Si_2O_5$ I, $Na_2Si_2O_5$ I, $Na_2Si_2O_5$ II	678	25.0	16.3	58.7
G	”	Na_2SiO_3, $Na_2Si_2O_5$ I, $Na_2Si_2O_5$ II	678	22.0	19.5	58.5
H	”	$K_2Si_2O_5$ I, $Na_2Si_2O_5$ I, $Na_2Si_2O_5$ II	678	23.6	13.7	62.7
J	”	Quartz I, $Na_2Si_2O_5$ I, $Na_2Si_2O_5$ II	678	14.4	15.4	70.2

*For a crystallographic description of the compounds see Refs. 1, 2, and 3.

TABLE II (Continued)
Invariant Points*

	Type	Crystal phases in coexistence with liquid	t°C	Composition of liquid weight per cent		
				K°O	Na_2O	SiO_2
K	Inversion	$Na_2Si_2O_5$ II, $K_2Si_2O_5$ I, $K_2Si_2O_5$ II	596	22.9	9.3	67.8
L	”	Quartz I, $K_2Si_2O_5$ I, $K_2Si_2O_5$ II	596	24.6	5.7	69.7
M	”	$K_2Si_2O_5$ II, Quartz I, Quartz II	573	23.8	6.5	69.7
N	”	$Na_2Si_2O_5$ II, Quartz I, Quartz II	573	20.6	9.8	69.6
O	Reaction	$K_2Si_4O_9$ I, $K_2Si_2O_5$ II, Quartz I	640	25.7	4.5	69.8
P	Inversion	Quartz I, Tridymite I	870	25.6	—	74.4
Q	”	Quartz I, Tridymite I	870	—	24.5	75.5
R	”	Tridymite I, Cristobalite I	1470	10.5	—	89.5
S	”	Tridymite I, Cristobalite I	1470	—	11.3	88.7
T	Eutectic	$K_2Si_2O_5$ I, Na_2SiO_3	680	28.7	17.6	53.7
U	Unmixing	$K_2Si_2O_5$ I and mixed crystals	923	36.8	5.5	57.7
V	”	$Na_2Si_2O_5$ I and mixed crystals	742	10.3	26.0	63.7
—	Melting	K_2SiO_3	976	61	—	39
—	”	Na_2SiO_3	1089	—	50.8	49.2
—	”	$K_2Si_2O_5$	1036	43.95	—	56.05
—	”	$Na_2Si_2O_5$	875	—	34.04	65.96
—	”	$K_2Si_4O_9$	765	28.16	—	71.84
—	”	Cristobalite	1713	—	—	100

* For a crystallographic description of the compounds see Refs. 1, 2, and 3.

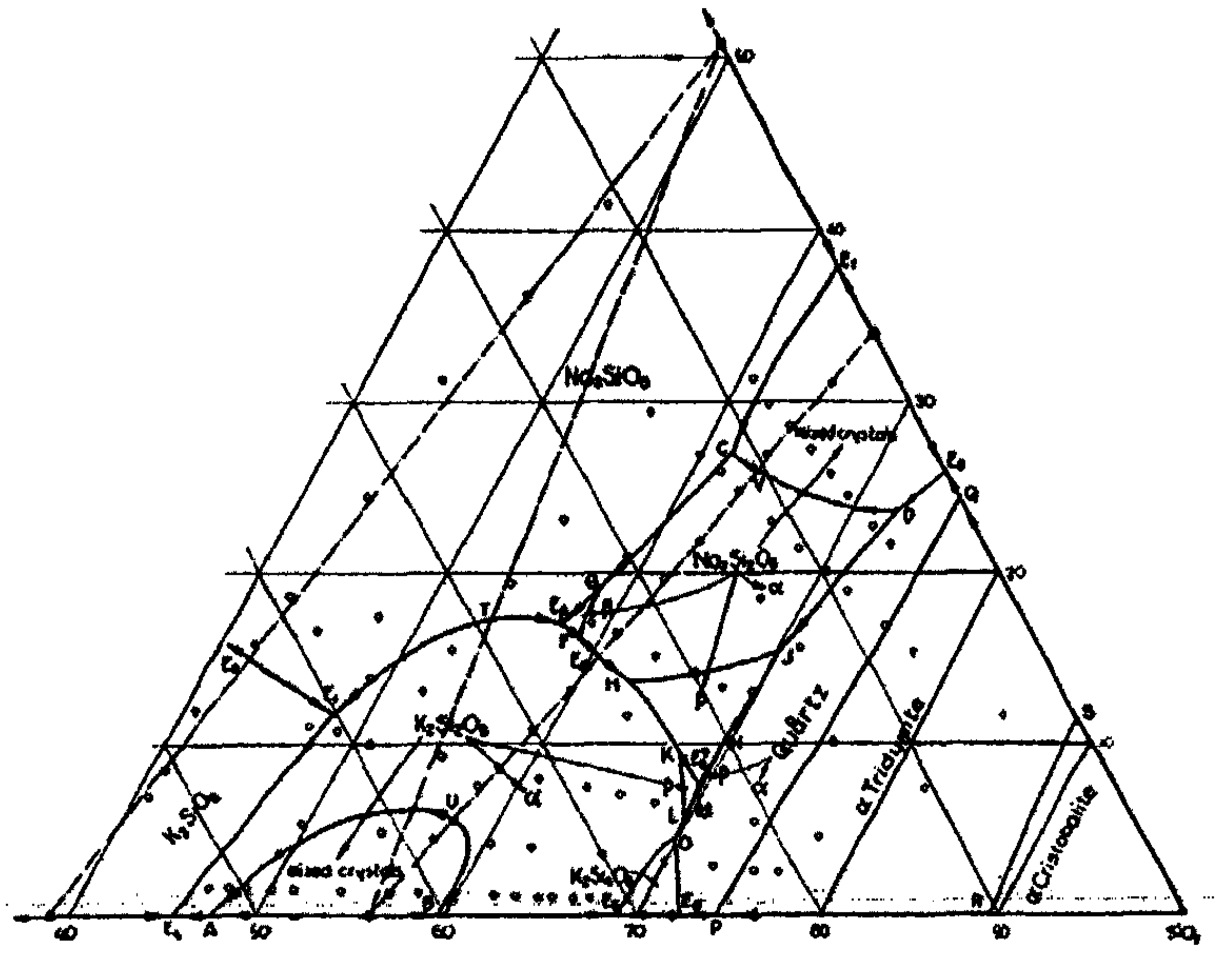

Fig. 1

The ternary system, K_2SiO_3-Na_2SiO_3-SiO_2. This figure shows the compositions of the mixtures studied represented by open circles; the compositions of the binary potassium and sodium silicates by black circles, and the fields of the compounds.

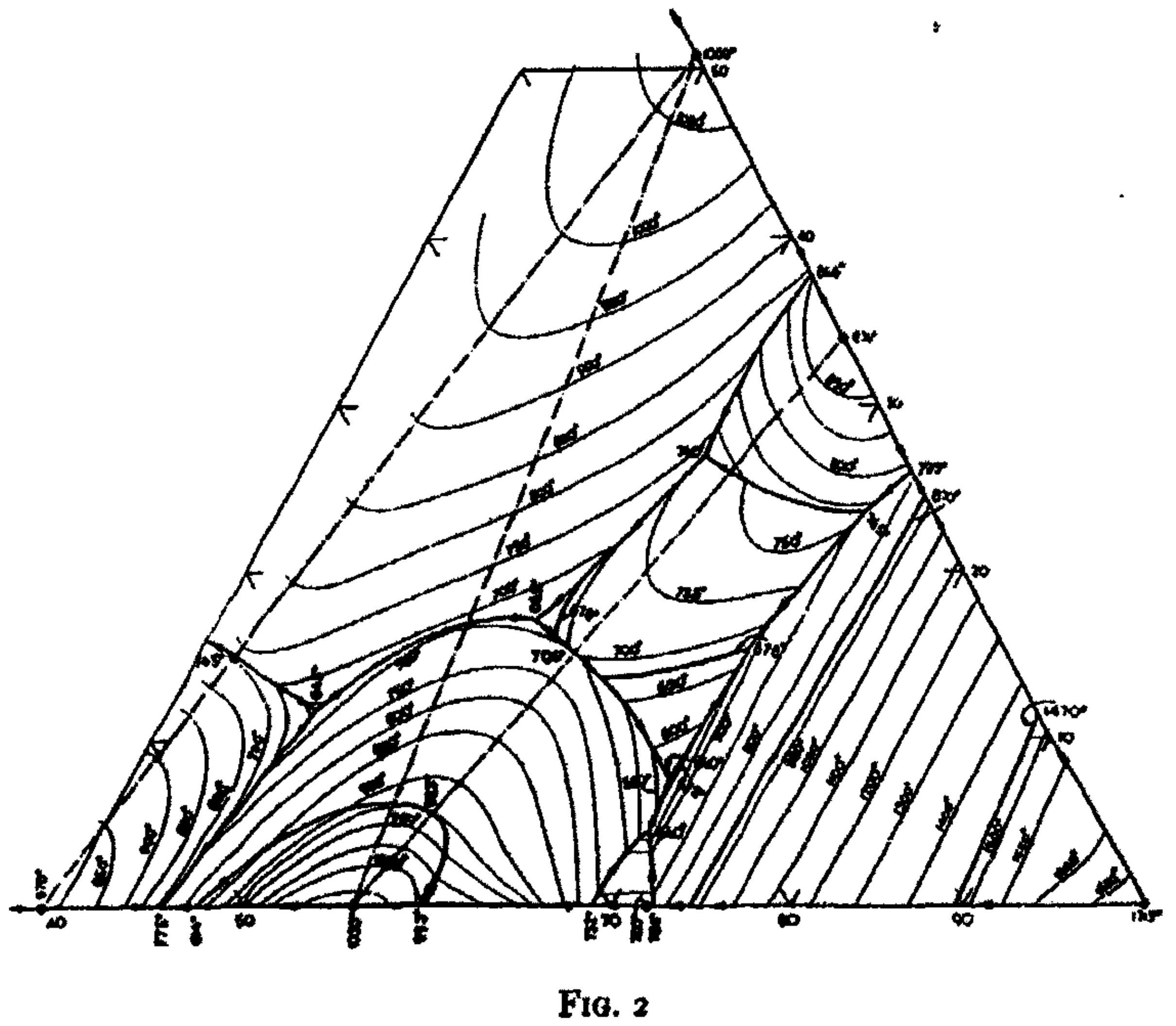

Fig. 2

The ternary system, K_2SiO_3-Na_2SiO_3-SiO_2. This diagram shows the isotherms of the liquidus surfaces of the various compounds.

Discussion of the Ternary System

The equilibrium diagrams of Figs. 1 and 2 present the stability fields of the crystalline compounds occurring in the system. It will be seen by reference to the figures that there are no ternary compounds and no incongruent melting relations between the adjacent binary compounds, hence the system is one of comparative simplicity. The only complications entering are due to the unique type of solid solution relations of the disilicates, and the polymorphic relations of the compounds, $Na_2Si_2O_5$, $K_2Si_2O_5$, and the various modifications of silica, namely, high and low quartz (Quartz I and II), tridymite, and cristobalite.

In addition to the component binary systems along the binary boundaries there are three binary systems within the ternary system, K_2SiO_3-Na_2SiO_3-SiO_2, namely, K_2SiO_3-Na_2SiO_3, $K_2Si_2O_5$-$Na_2Si_2O_5$, and $K_2Si_2O_5$-Na_2SiO_3. Two other possible binary systems, K_2SiO_3-$Na_2Si_2O_5$ and $K_2Si_4O_9$-$Na_2Si_2O_5$, fail to appear. The first of these is excluded by the existence of the binary system, $K_2Si_2O_5$-Na_2SiO_3, the second fails to be realized at the liquidus as a consequence of the excessive area covered by the liquidus surface of $K_2Si_2O_5$.

The melting relations for the ternary system accordingly are composed of the liquidus surfaces of K_2SiO_3, Na_2SiO_3, $K_2Si_2O_5$, $Na_2Si_2O_5$, $K_2Si_4O_9$, quartz, tridymite, and cristobalite. The ternary system may be thought of in terms of three subsidiary ternary systems: (1) K_2SiO_3-Na_2SiO_3-$K_2Si_2O_5$, with a ternary eutectic at 40.1 wt. per cent K_2O, 11.7 wt. per cent Na_2O and 48.2 wt. per cent SiO_2, 645°C; (2) $K_2Si_2O_5$-Na_2SiO_3-$Na_2Si_2O_5$, with a ternary eutectic at 25.4 wt. per cent K_2O, 17.2 wt. per cent Na_2O, and 57.4 wt. per cent SiO_2, 665°C; (3) $K_2Si_2O_5$-$Na_2Si_2O_5$-SiO_2 (Quartz II), with a ternary eutectic at 22.9 wt. per cent K_2O, 7.6 wt. per cent Na_2O and 69.5 wt. per cent SiO_2, 540°C. A list of the various invariant points encountered in the system is given in Table II; Figs. 3 and 4 represent the binary systems, K_2SiO_3-Na_2SiO_3 and $K_2Si_2O_5$-$Na_2Si_2O_5$. The binary system, $K_2Si_2O_5$-Na_2SiO_3, was not separately investigated, and hence is not represented.

The liquidus surfaces of K_2SiO_3 and Na_2SiO_3 are simple curved sheets and need no further discussion.

The liquidus surfaces of the different varieties of silica rise steeply in succession from the ternary eutectic for $K_2Si_2O_5$, $Na_2Si_2O_5$, and quartz II at 540°, with inversion boundaries 573° for quartz II and quartz I, 870° for quartz I and tridymite, 1470° for tridymite and cristobalite. The stability relations for the different varieties of silica are those determined by Fenner.[9] The liquidus surface for cristobalite necessarily exhibits a fold in consequence of the difference in the liquidus curves for cristobalite in the component-binary systems, K_2O-SiO_2 and Na_2O-SiO_2, the curve in the latter system exhibiting a reverse S curvature. The liquidus surfaces of tridymite, quartz I and quartz II are smooth sheets with no special features. The low ternary eutectic temperature for $K_2Si_2O_5$ II, $Na_2Si_2O_5$ II, and quartz II is noteworthy. This was investigated by the method employed by Morey and Bowen in their study of the system, Na_2SiO_3-$CaSiO_3$-SiO_2.[10] Crystallized

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[9] C. N. Fenner: Am. J. Sci., 36, 331 (1913).

[10] Morey and Bowen: J. Soc. Glass Tech., 9, 226 (1925).

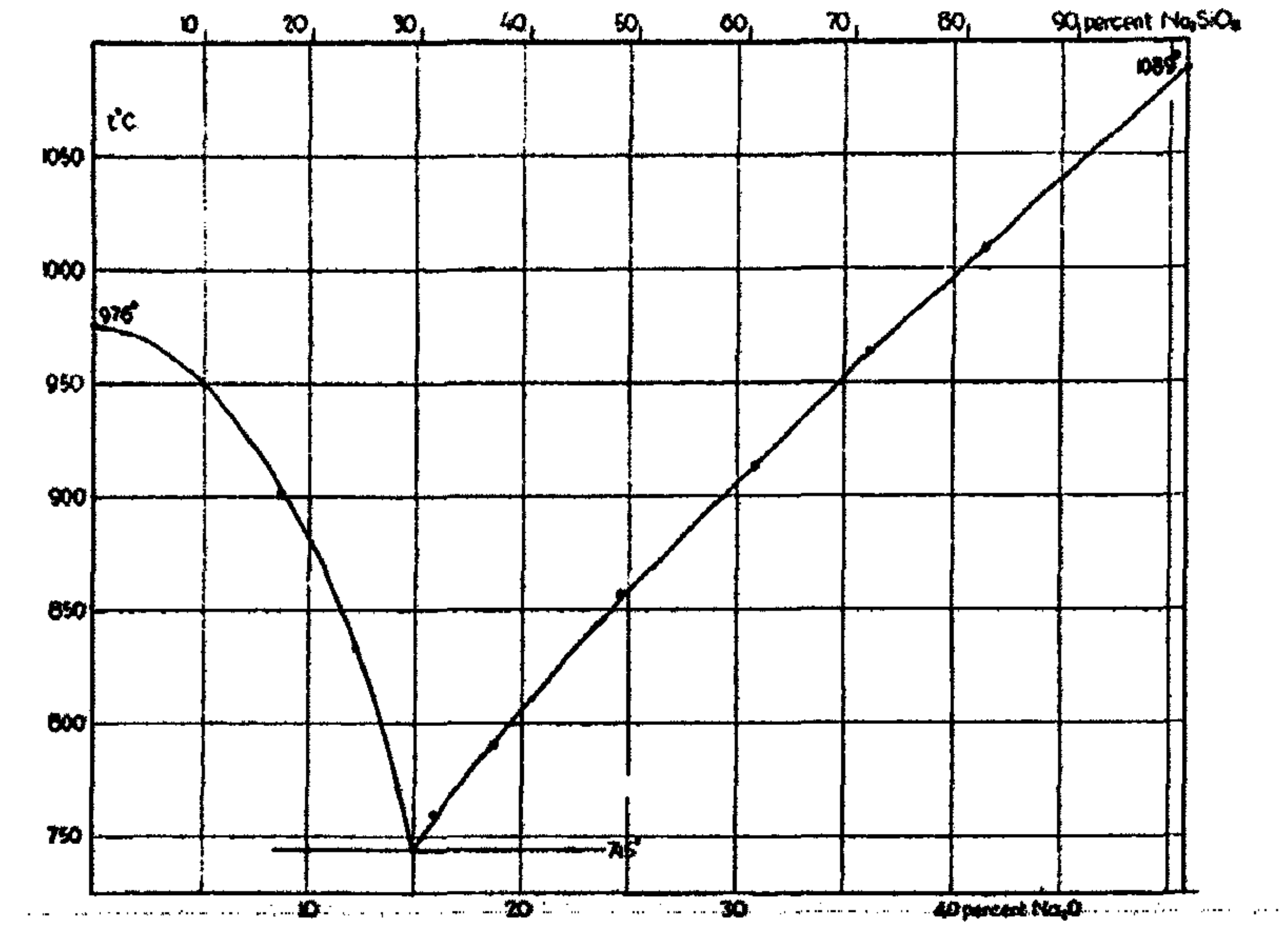

Fig. 3
Section through ternary diagram, showing the binary system, K_2SiO_3-Na_2SiO_3.

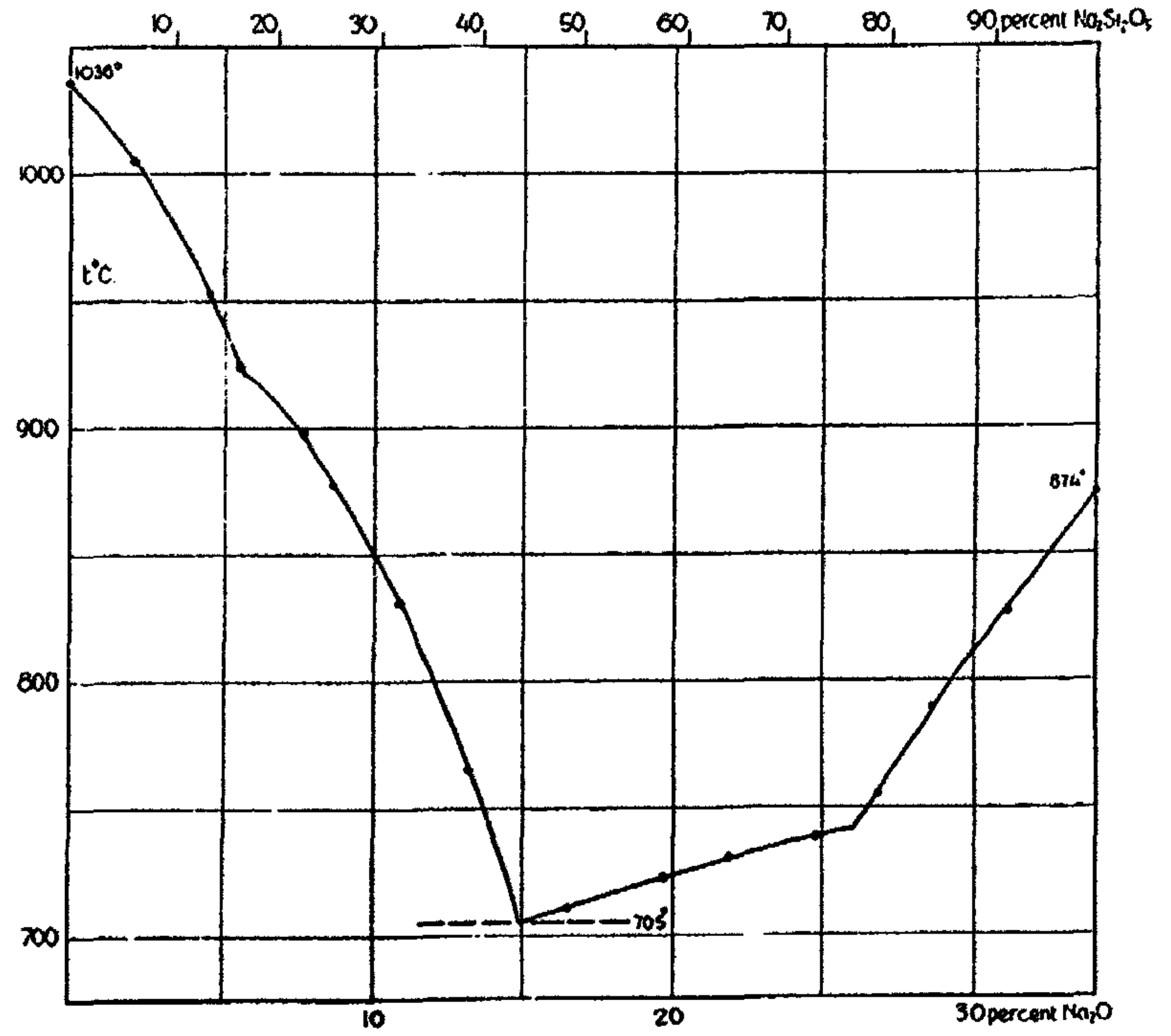

Fig. 4
Section through ternary diagram, showing the binary system, $K_2Si_2O_5$-$Na_2Si_2O_5$.

$Na_2Si_2O_5$, $K_2Si_2O_5$, and extremely finely powdered quartz were ground together in the required proportions and samples of the mixtures were held at various constant temperatures to determine the point at which sintering and glass formation take place. The most probable value thus determined is 540°C; the uncertainty is about ±30°C. The reactions between silicates at such low temperatures are extremely slow, and even 5 to 10 days heating at a given temperature above the eutectic does not serve to completely dissolve quartz crystals.

The field of $K_2Si_4O_9$ occupies only a small portion of the ternary diagram. This compound exists in two polymorphic modifications with an inversion at 592° at the pressure of 1 atmosphere.[11] The lowest liquidus temperature with $K_2Si_4O_9$ as the stable phase in the ternary system is 640° for the equilibrium between $K_2Si_4O_9$ I, $K_2Si_2O_5$ I, quartz I and liquid, and hence the low temperature modification, $K_2Si_4O_9$ II does not reach the liquidus.

The disilicates, $K_2Si_2O_5$ and $Na_2Si_2O_5$, present interesting features. Reference to Fig. 4 shows that the liquidus curves of both these compounds in their binary system exhibit breaks, at 920° for $K_2Si_2O_5$, and at 742° for $Na_2Si_2O_5$. Reference to the work on the binary systems, K_2SiO_3-SiO_2 and Na_2O-SiO_2[1,2] reveals that in the potash system corresponding breaks are encountered at 814° on the K_2O side, and at 993° on the SiO_2-side of the $K_2Si_2O_5$ composition. In the soda system heat effects were located at 706° on the Na_2O side, and at 768° on the SiO_2 side of the $Na_2Si_2O_5$ composition, below the liquidus temperatures throughout. The interpretation was that both $K_2Si_2O_5$ and $Na_2Si_2O_5$ enter into solid solutions with excess SiO_2, and excess K_2O and Na_2O respectively, the different temperatures established being the unmixing temperatures of these solid solutions. Below the unmixing temperatures the crystals are essentially the pure disilicates, as evidenced by the constancy of inversion temperatures, 596°C for $K_2Si_2O_5$ I and $K_2Si_2O_5$ II, and 678° for $Na_2Si_2O_5$ I and $Na_2Si_2O_5$ II.

In the ternary system a search was made for the existence of possible compounds which might explain the presence of the above-mentioned breaks at 920° and 742° in the subsidiary binary system, $K_2Si_2O_5$-$Na_2Si_2O_5$. This search revealed that no such compounds exist, but that the unmixing boundaries AB and CD (Fig. 1) are not constant temperature lines; they are screw curves, the temperature rising continuously from A, 814°C to B at 992°C, the intersection of the screw curve with the disilicate join being at 920° at U, for the $K_2Si_2O_5$; in the case of the $Na_2Si_2O_5$ the screw curve is entirely within the ternary system, rising from C at 740° through V at 742° to D at 765°, the two ends of the screw curve being at 706° and 768° respectively, under the liquidus surface. The unmixing and the polymorphic inversions in these two compounds are prompt, hence no definite optical evidence for the existence of the solid solutions is adducible. In the case of the $Na_2Si_2O_5$ a slight modification of the external form of the crystals was noticed, but this was not sufficient for a description. The relations may then be summarized in the statement that both $Na_2Si_2O_5$ and $K_2Si_2O_5$ take up limited excess of SiO_2,

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[11] Goranson and Kracek: J. Phys. Chem., 36, 913 (1932).

Na_2O, or K_2O, respectively, depending on the composition of the liquid from which they crystallize, in the component-binary systems, and that $K_2Si_2O_5$ takes in a limited amount of Na_2O, while $Na_2Si_2O_5$ takes in a limited amount of K_2O in the ternary system under description.

In addition to the above-described solid solution phenomena, the liquidus surfaces of $K_2Si_2O_5$ and $Na_2Si_2O_5$ show the inversion temperatures $K_2Si_2O_5$ I to $K_2Si_2O_5$ II at 596° and $Na_2Si_2O_5$ I to $Na_2Si_2O_5$ II at 678°.

The temperatures of the eutectics E_1 and E_2, namely $K_2SiO_3 + K_2Si_2O_5$ I + Na_2SiO_3 + L and $K_2Si_2O_5$ I + Na_2SiO_3 + $Na_2Si_2O_5$ II + L, were determined by quenching previously crystallized preparations heated at the various appropriate constant temperatures and examining with the microscope for the first appearance of glass. The compositions employed for this purpose were Nos. 53 and 95 for E_1 and 12 for E_2. The compositions used do not melt completely at the eutectic temperatures. These eutectic temperatures were located with an uncertainty of ±10°, the uncertainty being due to the difficulty of recognizing the first traces of glass in the microscopic examination.

From the physical-chemical point of view it is of interest to note that the liquidus surfaces of the silicate compounds of the system are sheets with very flat maxima at the melting points, and generally with a large radius of curvature. This indicates considerable dissociation of these silicates in the liquid state.[12] The extensive dissociation of the liquid is also indicated by the relatively low melting points, with the statistical implication that the silicates are not definite compounds in the melts, particularly at higher temperatures. The situation is, in a sense, analogous to that encountered with other additive compounds; for example, while $CaCl_2.6H_2O$ undoubtedly is present in $CaCl_2$-H_2O solutions in appreciable amounts at the melting point of $CaCl_2.6H_2O$, it is probable from the point of view of statistical mechanics that the number of molecules of H_2O associated with one of $CaCl_2$ (or Ca^{++}) in solution depends upon average distribution governed by the intermolecular forces in the liquid, rather than upon the definite distribution governed by the directional forces in the lattice of a crystal.

Summary

The melting point relations in the ternary system, K_2SiO_3-Na_2SiO_3-SiO_2, are simply-eutectoid with respect to the component-binary systems, K_2SiO_3-SiO_2 and Na_2SiO_3-SiO_2, there being no ternary compounds. A unique type of solid solution formation is encountered in the disilicate region, both $K_2Si_2O_5$ and $Na_2Si_2O_5$ taking up a varying limited excess of the three constituents, K_2O, Na_2O, SiO_2, dependent upon the composition of the liquid in equilibrium with the crystals. The equilibrium diagrams of Figs. 1 and 2 present the phase relations worked out by the method of quenching, the data being given in Tables I and II.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1932.

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[12] W. Stortenbeker (upon suggestions of H. A. Lorentz): Z. physik. Chem., **10**, 183, 194 (1892), discussed by Lewis and Randall: "Thermodynamics," 217 (1923); see also A. Smits: Z. physik. Chem., **78**, 708 (1912); Morey and Bowen: Ref. 3; J. W. Gibbs: "Scientific Papers," **1**, 135.

THE EFFECT OF X-RADIATION ON THE VISCOSITY OF GELATINE*

BY HELEN QUINCY WOODARD

Introduction

The effect of various types of radiation on a number of organic and inorganic colloids has been reported in the literature. Fernau,[1] Fernau and Pauli,[2] Crowther and Fairbrother,[4] Fairbrother,[3] and Crowther[5] have made a thorough study of the effect of different types of radiation on ceric hydroxide sols and other inorganic colloids. They found in general that positive sols could be coagulated or rendered less stable by β, γ or X-rays, while negative sols were relatively unaffected. The doses required to produce measurable effects were large. There is a difference of opinion among these authors as to the role of H_2O_2 as an intermediate in the process of coagulation.

In the study of the effect of radiation on organic colloids Fernau and Pauli[2] found that albumins were flocculated by β and γ radiation. Fairbrother[6] found that the viscosity of egg albumin was decreased permanently by large doses of X-rays, and Fernau and Pauli[7] found that β and γ radiation decreased the viscosity of gelatine. Fernau[8] found that the coagulation temperature of serum and egg albumin was lowered by radium radiation. Wels and Thiele[9] gave sub-therapeutic X-ray doses to globulin sols, and found that the radiation caused aggregation of the particles. Loiseleur[10] found that the radiation from radium caused the flocculation of gelatine.

A good deal of other work has been done on the effect of various types of radiation on different colloids, but, because of the complexity of the systems used or the unsatisfactory character of the methods of observation, the results admit of no definite interpretation. Even among the most clear-cut results, as those reviewed above, there is much conflict.

In the present work the effect of moderately hard X-rays on the viscosity of dilute gelatine solutions was studied. Gelatine was chosen for the investigation because it is an organic colloid the properties of which are well known from the work of Loeb and Wilson. Viscosity was chosen as the property to be observed in the hope that observations on viscosity change might throw some light on the effect of X-rays on living tissues. This seemed possible, since the swelling of tissues which have been exposed to X-rays may be due to a change in the viscosity of the cell contents.

Apparatus and Materials

The gelatine used was "Coignet" gelatine from Akatos, Inc., New York City. It was obtained in thick sheets, and gave a pH of about 5.2 when dissolved in water. The water used for preparing the sols was redistilled from

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* From the Huntington Fund for Cancer Research, Memorial Hospital, New York City.

$KMnO_4$ solution. Chemicals of "C.P." and "T.P." grade from Eimer and Amend were used throughout. The pH of the sols was determined colorimetrically to 0.1 pH by comparison with buffer standards from the LaMott Chemical Supply Co.

The sols were prepared by placing a weighed piece of dry gelatine in a flask, adding the required amount of water, HCl, or NaOH, placing the flask in a boiling water bath for exactly 5 min., removing the flask, shaking until the gelatine was dissolved, and then cooling with running cold water. The maximum temperature reached by the sol during 5 min. in the water bath was about 85°C. The time of shaking required to dissolve the gelatine was from ten to twenty minutes, and this difference in the time during which the sols were held at a high temperature accounted for considerable differences in the viscosity.

The sols were irradiated in crystallizing dishes 46-49 mm. in diameter covered by watch glasses 1.0-1.8 mm. thick. Thirty cc. samples were used. Sols irradiated in dishes with this range of diameters showed radiation effects identical within the experimental error. The X-ray setting was 200 K.V., 30 m.a., distance target to bottom of dish 42 cm., no filter, 40 min. exposure. The X-ray tube was of the new thick-walled type. The glass was about 5 mm. thick, and this was sufficient to filter out the softest radiation. The machine delivered about 270 roentgens per minute at this setting, so that the total dose amounted to about 10800 roentgens.

Viscosities were determined in an Ostwald viscometer immersed in a water bath with a temperature range of 24.7°-25.3°C. The viscometer was calibrated for 5 cc. of water for every tenth of a degree from 24.°0 to 26.°0 C. The temperature was noted for every viscosity reading on gelatine, and the relative viscosity of the gelatine was calculated as, relative viscosity = R.V. = time of delivery for gelatine at t° divided by time of delivery for water at t°. The water value of the viscometer at 25°C. was 78.3 sec. and successive values checked to ±0.1 sec. The water value was determined at least once a day. When the viscosity of a large number of gelatine sols was determined on the same day, the viscometer was cleaned with sulfuric and chromic acids and the water value checked after every eight determinations.

Successive readings on the same sample of gelatine gave readings identical to ±0.1 sec. with no drift that would suggest a structural viscosity. Tests were made with different volumes of sol, 3.0, 5.0, and 7.5 cc. These differences in volume caused the sols to flow under different pressures. The value for R.V. was found to change with pressure, and this showed that the viscosity was in fact structural. These tests were made on gelatine sols of pH 3.3-3.5 over a concentration range of 0.2%-1.0%.

Experimental

Preliminary work showed that the viscosity of gelatine sols was decreased by irradiation, and that the difference between irradiated and control sols was greater the greater the initial viscosity of the sol. The viscosity of a gelatine sol of given concentration may be changed by heat, by age, by the addition of salts, by change in pH and by irradiation. These viscosity changes are brought about by different changes in the structure of the colloid.

The effect of ageing at moderate temperatures (37°C. and below) is apparently the slow establishment of a reversible equilibrium between α and β gelatine, which possess different colloidal properties. The effect of more severe heating is an irreversible disaggregation of the gelatine micelles, with great decrease in viscosity, but without change in chemical properties unless the heating is very prolonged.[14] The two types of change are probably closely connected. The addition of salts lowers the viscosity by changing the degree of swelling of the colloidal micelles through the well-known Donnan equilibrium effect. Change in pH also alters the viscosity through change in the Donnan equilibrium, and, in addition, changes the degree of ionization of the gelatine. The nature of the change brought about by irradiation is unknown.

A study was made of the differences in the effect of radiation on gelatine sols the viscosity of which had been changed in these five ways. In addition, differences in the effect of radiation on sols of different concentration were studied.

As it was not possible to make up successive sols of the same concentration and pH value which had the same viscosity, such sols could not in general be plotted on the same curve. In order to obtain a direct comparison between two or more sols it was necessary to take the initial relative viscosity of the control samples as 100%. Subsequent values of the control and experimental samples were then calculated as percent of this initial value. In this way figures for successive experiments could be compared directly, provided the initial viscosities did not differ too greatly. Sols of very different initial viscosities could not be compared by this method, however, since the percentage change in viscosity produced by a given quantity of radiation was greater the more viscous the sol.

In most of the work it was necessary to compare sols of different initial viscosities. In this work the viscosity of the control samples, $R.V._{.c}$, was plotted directly against the percent reduction of viscosity produced by radiation, $\frac{R.V._{.c} - R.V._{.e}}{R.V._{.c}}$. In each of these experiments different portions of the same sols were treated in different ways and irradiated at the same time. Where a series of such sols is plotted on the same figure, the points representing percent reduction in viscosity of the untreated portion of each sol are plotted thus (x); points representing percent reduction of viscosity of the treated portions of the sol are represented thus (.). The degree of scattering of the points representing untreated sols is a measure of the experimental error and of the variations in the material used. Where the width of the band defined by points for the treated sols is not greater than that of the portion of the band defined by the points for the initial sols, it is considered that the effects observed are produced by the treatment and are not the result of experimental error.

Since differences in the temperature at which gelatine sols are kept produce permanent changes in viscosity, all sols were kept at the same temperature (25°C.) except while the experimental sols were being irradiated. During this period the control sols were kept at room temperature. The difference between the temperatures of liquids in the X-ray chamber and in the room outside the chamber did not exceed 3°C. In order to determine whether either this slight change in temperature or the ozone and oxides of nitrogen produced by the X-rays would affect the viscosity of gelatine, sols were placed in a part of the chamber which was shielded from radiation, and the machine was operated for 40 minutes. No significant difference was observed between sols so treated and sols kept at room temperature. A further test of the temperature effect was made by placing a portion of a sol in the 37°C. incubator for one hour and then returning it to the 25°C. incubator where the control was kept. A small reduction in the relative viscosity (0.7%) was observed, which persisted for 48 hours. As the temperature difference used here was four times as large as that which was found following irradiation, and as the viscosity change was much smaller than most of the changes observed after irradiation, it is felt that temperature changes in the gelatine sols in the X-ray chamber produced no significant differences in the results.

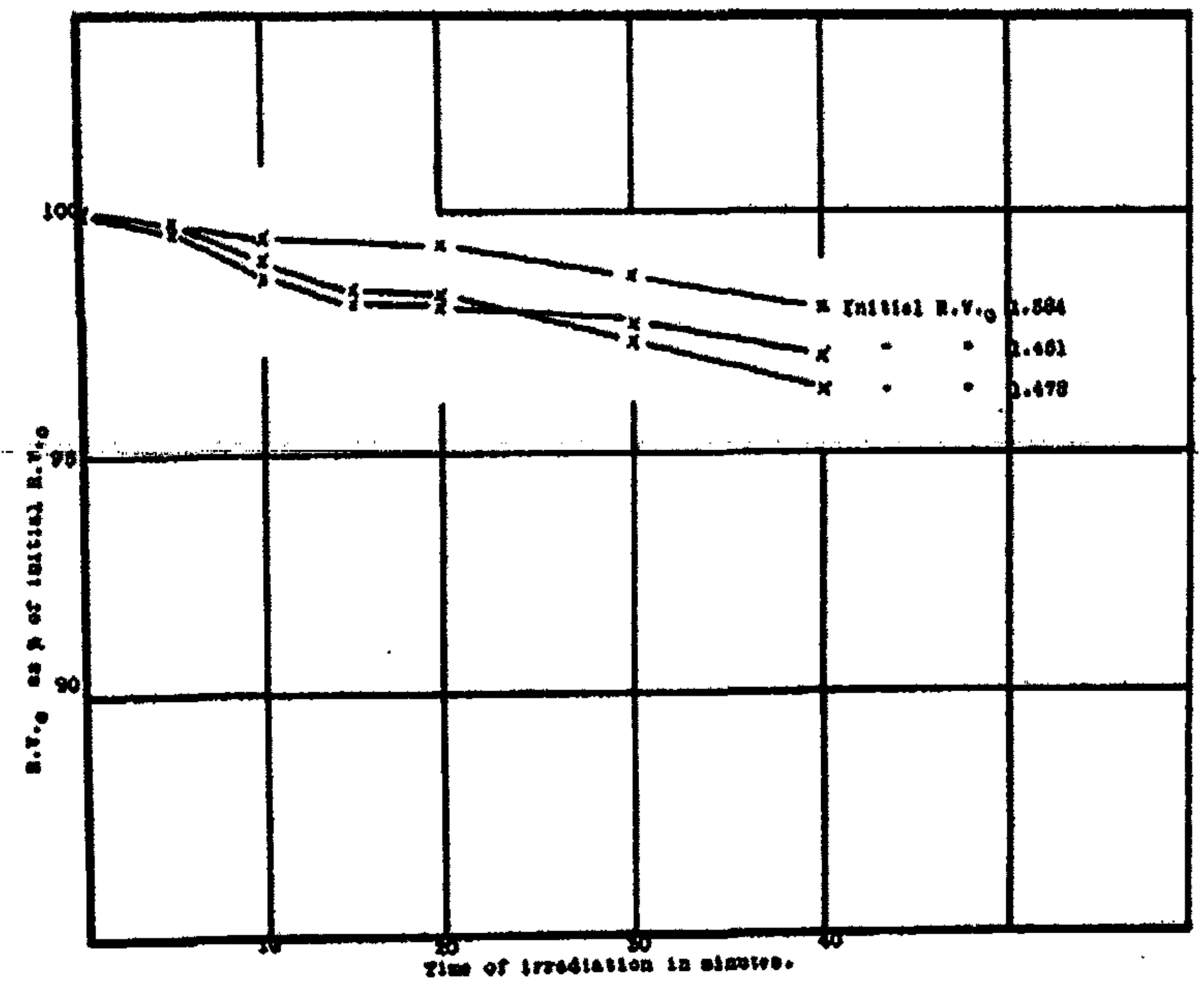

Fig. 1

Change of Viscosity with Time of Irradiation

The effect of different doses of radiation delivered to portions of the same sol within a one hour period is shown in Fig. 1. The radiation effect increases fairly regularly with time of irradiation but is not directly proportional to time. The figure also illustrates the difference in the radiosensitivity of sols with different initial viscosities. The two sols for which the relative viscosity of the controls 24 hours after irradiation were 1.451 and 1.477 showed a reduction of these viscosities of 3.0% and 2.7% respectively, while the sol for which the relative viscosity of the control was only 1.384 has this value reduced by only 2%.

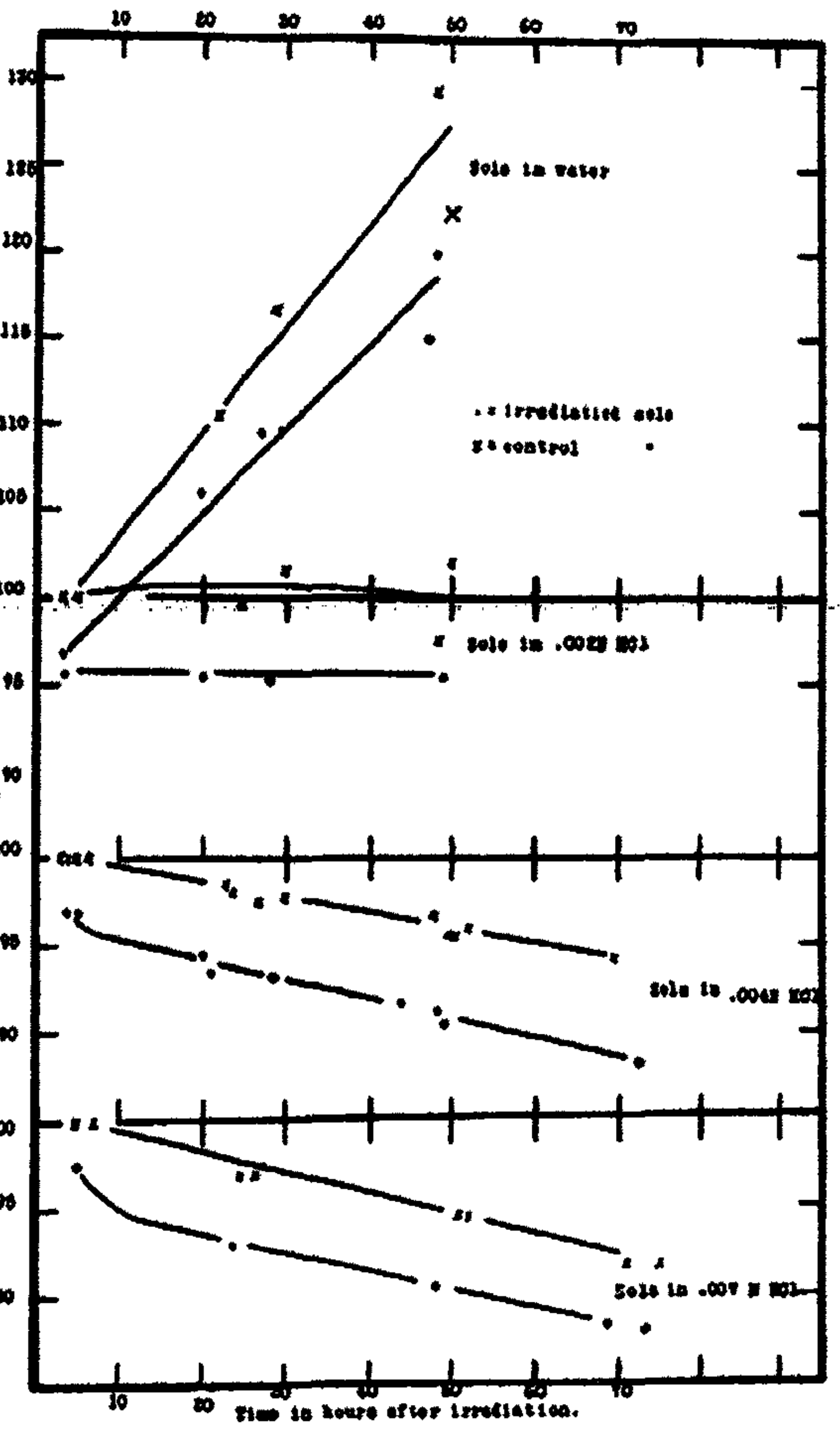

FIG. 2
Change of Viscosity with Time

The change in the radiation effect with time after irradiation is shown in Fig. 2. This shows the relative viscosities of irradiated and control sols containing 0.4% gelatine dissolved in water and in 0.002 N HCl, 0.004 N HCl, and 0.007 N HCl at different times after irradiation, all values being calculated as percent of the values for the controls on the day of irradiation. It is seen that the difference between irradiated and control sols is approximately constant after 24 hours. The viscosity of both irradiated and control sols of pH greater than 3.8 rises with time; that of sols with a lower pH falls with time. The curves for sols in 0.001 N HCl, 0.003 N HCl, 0.005 N HCl, and 0.006 N HCl occupy positions intermediate with those shown in the figure, while those for sols in 0.008 N HCl, 0.009 N HCl and 0.010 N HCl are similar to those for sols in 0.007 N HCl.

In the subsequent work the radiation effects reported are values for irradiated and control sols read 20-30 hours after irradiation. It is felt to be more satisfactory to compare the values for $\mathrm{R.V.}_c$ and $\mathrm{R.V.}_e$ at the same time, rather than to compare the values for $\mathrm{R.V.}_e$ with the R.V. of the controls at the time of irradiation, since the former method is not confused by the changes which both irradiated and control sols undergo with time. Unless otherwise stated, all the irradiated sols in the subsequent work were irradiated for 40 minutes.

Effect of Heat

Fig. 3 shows the effect of heat on the radiosensitivity of 0.4% gelatine sols in 0.004 N HCl, pH 3.3. The initial sols were made up in the usual way by heating for 5 min. on the water bath and shaking until the gelatine was all dispersed. Samples were then withdrawn while the sol was still hot and cooled immediately, the remainder being put back in the water bath for different periods up to 90 min. The initial sols reached a temperature of 86° in 5 min. The maximum temperature observed in subsequent heatings was 94°. Half of each sample was then irradiated and the remainder kept as a control. The wide range of the abscissas in the figure shows that the relative viscosities of the controls were greatly reduced by heat.

In the figure the percent reduction of the relative viscosity of each irradiated sample $\frac{\mathrm{RV.}_c - \mathrm{R.V.}_e}{\mathrm{R.V.}_c}$ is plotted against the relative viscosity of its control, $\mathrm{R.V.}_c$. It is seen that the radiation effect decreases with decreasing relative viscosity of the controls and reaches zero for a sol for which $\mathrm{R.V.}_c = 1.073$. Initial sols are marked (x); sols heated for longer periods than 5 min. are marked (.). The variation of the heated sols is not greater than that of the controls.

It is probable that gelatine when heated for 90 min. at 90°C. is almost entirely converted into the β form. Since these heated sols were not radiosensitive, it appears that under the conditions employed in the present work, it is only the α form which is sensitive to X-rays.

Effect of Added Salts

Fig. 4 shows the effect of added salts on the viscosity and radiosensitivity of 0.4% gelatine in 0.004 N HCl. Eight-tenths percent sols in 0.008 N HCl were made up and then diluted to 0.4% with solutions of different salts so that the final salt concentration was 0.004 N. The salts were used NaCl, KCl, Na_2SO_4, $HgCl_2$, KH_2PO_4, K_2CrO_4, $NaNO_2$, $NaNO_3$, NH_4Cl, $(NH_4)_2SO_4$. Sols without added salts are plotted thus (x); sols with added salts are plotted thus (.). The relative viscosity of the controls was reduced by the addition of salts in the manner to be expected from the Donnan equilibrium relations.

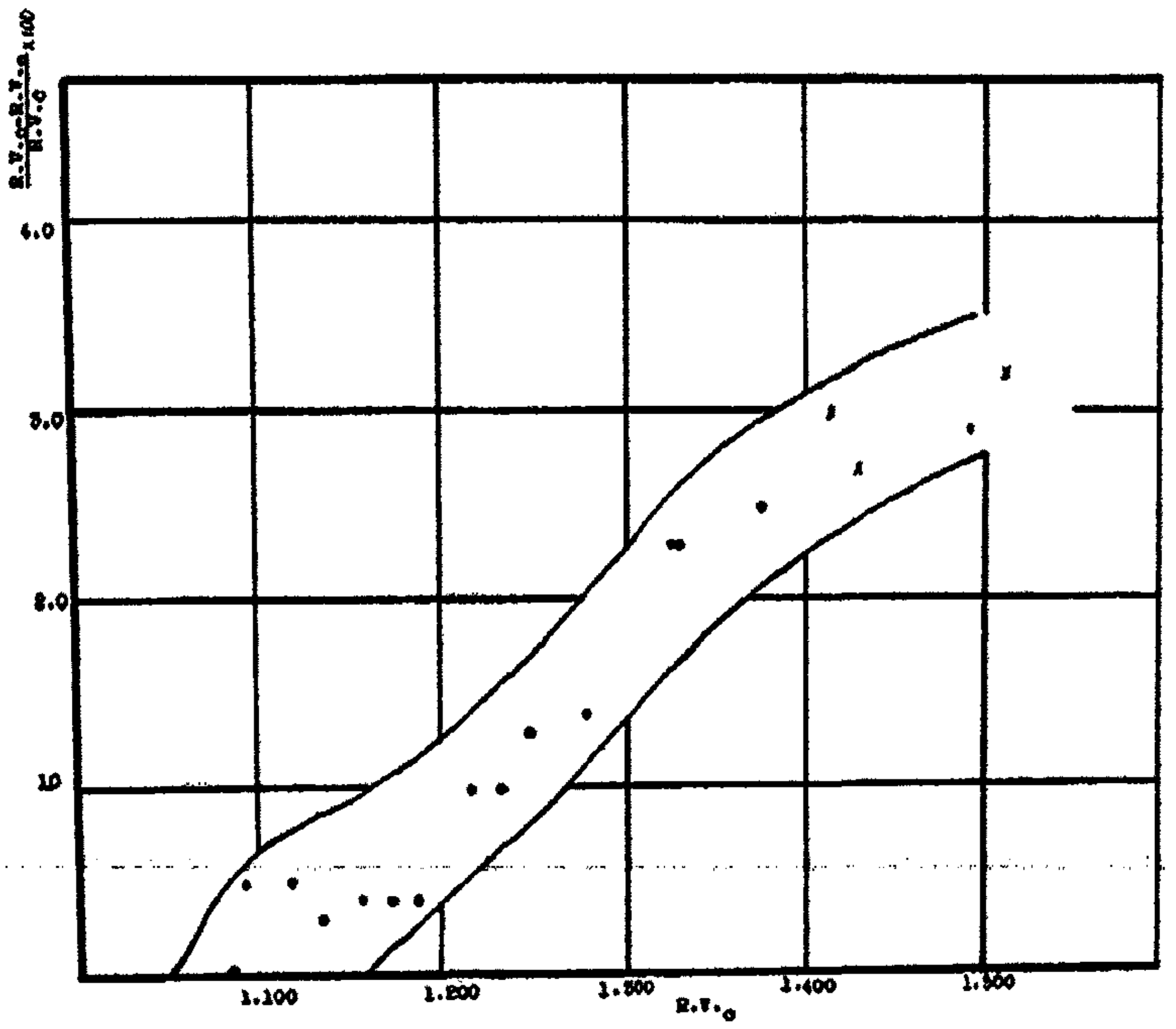

FIG. 3
Effect of Heat on Radiosensitivity

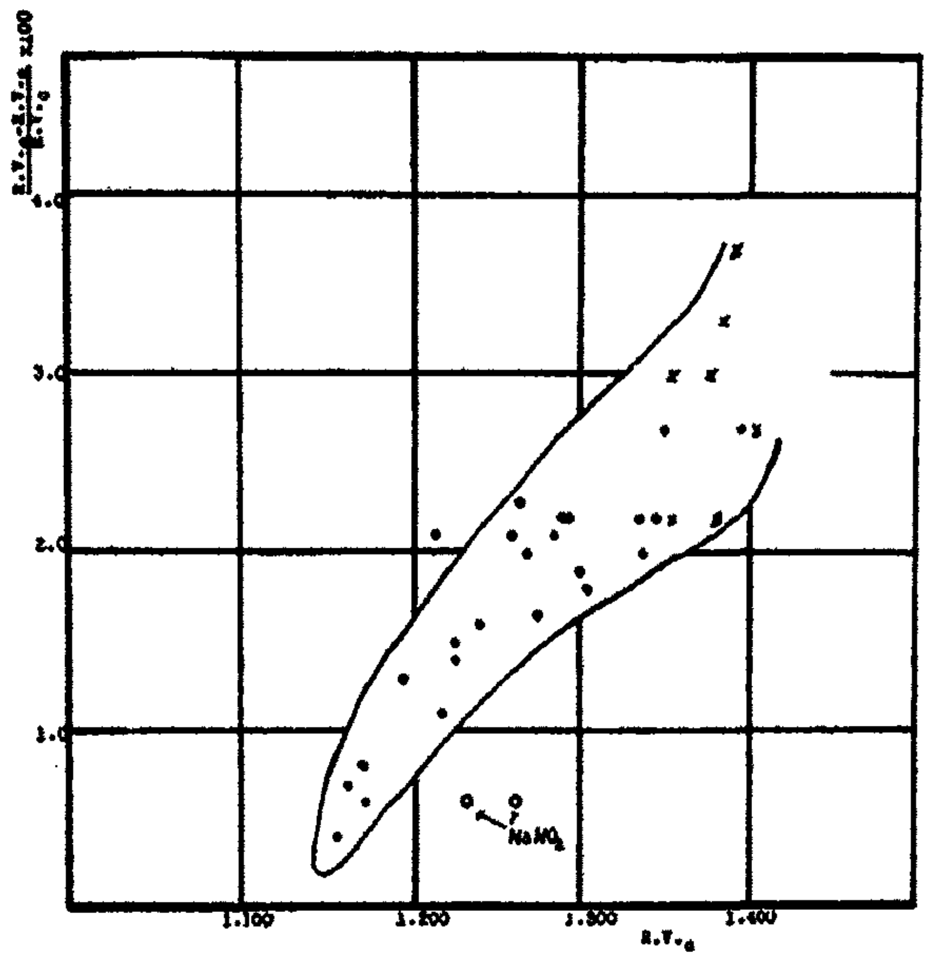

FIG. 4
Effect of added Salts on Radiosensitivity

It is seen that, when the relative viscosity of the gelatine is decreased by the addition of salts the radiosensitivity is also decreased. With the exception of sols to which $NaNO_2$ has been added, the variation of the treated sols is not greater than that of the controls. The disproportionately great reduction in radiosensitivity brought about by $NaNO_2$ is probably due to the fact that nitrous acid, which is liberated from the nitrite in acid solution, reacts chemically with the gelatine. The effect of this salt is therefore more than a simple change in Donnan equilibrium.

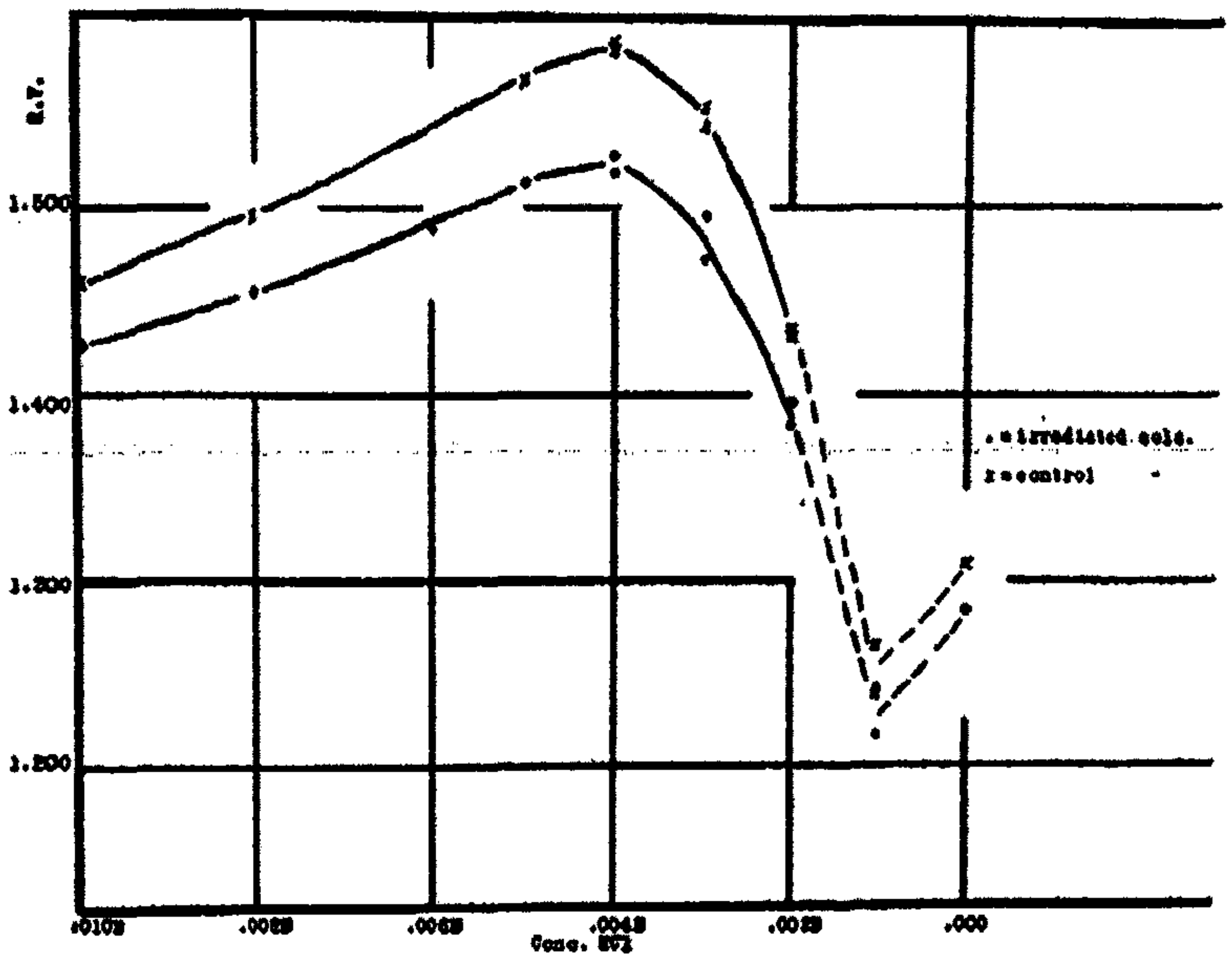

Fig. 5
Effect of pH on Viscosity and Radiosensitivity

The addition of none of these salts altered the pH of the sols more than 0.2 pH. Slight changes in pH in the neighborhood of pH 3.3 do not alter the radiosensitivity, as is shown in the subsequent section.

Effect of pH

Eight-tenths percent gelatine sols were made up in water. Several portions of each sol were then diluted to 0.4% with HCl of different concentrations. Half of each sample was then irradiated, the remainder being kept as a control. Two of these sols were so nearly of the same initial concentration that they could be plotted directly on the same curve. Fig. 5 shows the relative viscosities of irradiated and control samples of these sols plotted against concentration of HCl. It is seen that, in general, the radiation effect as shown by the distance between the two curves is greater for the more viscous sols. A sol of given viscosity on the acid side of pH 3.3 is less sensitive than one on the alkaline side however. In Fig. 6, the relative viscosity of the controls is plotted against the percent reduction of relative viscosity of the experimental sols for sols of pH 3.3 or less. It is seen that the radiosensitivity decreases with decreasing relative viscosity. The same effect was observed for sols of pH greater than 3.3, but the experimental error was too large for definite conclusions. The difference in the behavior of sols on the acid and alkaline sides of the point of maximum viscosity shows that some other factor than viscosity affects the radiosensitivity.

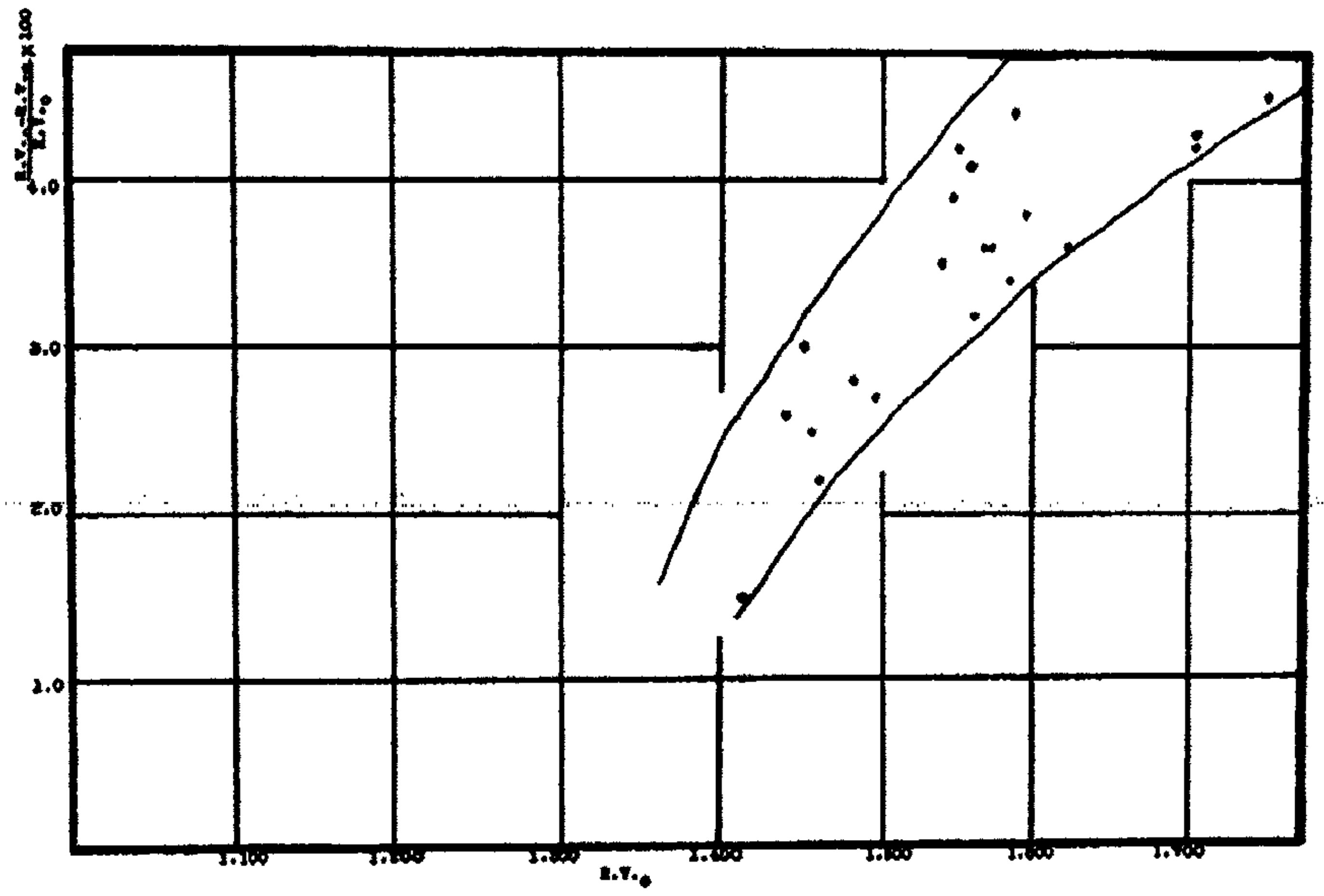

Fig. 6
Effect of pH on Radiosensitivity

Effect of Time

The relative viscosity of 0.4% gelatine of pH 3.3 decreases with time as was shown above; that of 0.4% gelatine of pH 5.6 increases with time. If it is true in general that radiosensitivity is a function of viscosity, then we should expect the radiosensitivity of gelatine of pH 3.3 to decrease with time and that of gelatine of pH 5.6 to increase with time. It was found that the radiosensitivity of gelatine of pH 3.3 does in general decrease with time, although the experimental error is too large for satisfactory quantitative work. No quantitative work was possible with sols of pH 5.6, as these nearly isoelectric sols are extremely variable.

Effect of Previous Irradiation

Since the viscosity of gelatine is reduced by radiation, it is interesting to determine whether this reduction in viscosity is accompanied by a reduction of sensitivity to further irradiation. The experiment is complicated by the fact that the radiation effect increases for at least 24 hours after exposure. Hence it is necessary to irradiate different portions of a sol at 24 hour intervals.

The radiosensitivity of each portion is then determined by comparing its viscosity 24 hours after the last irradiation with that of the sample which has received one less exposure. This prolongs the experiment and so increases the experimental error that the results are not clear cut. In general, however, it is found that, when the viscosity is reduced by irradiation, the sensitivity to further irradiation is also reduced.

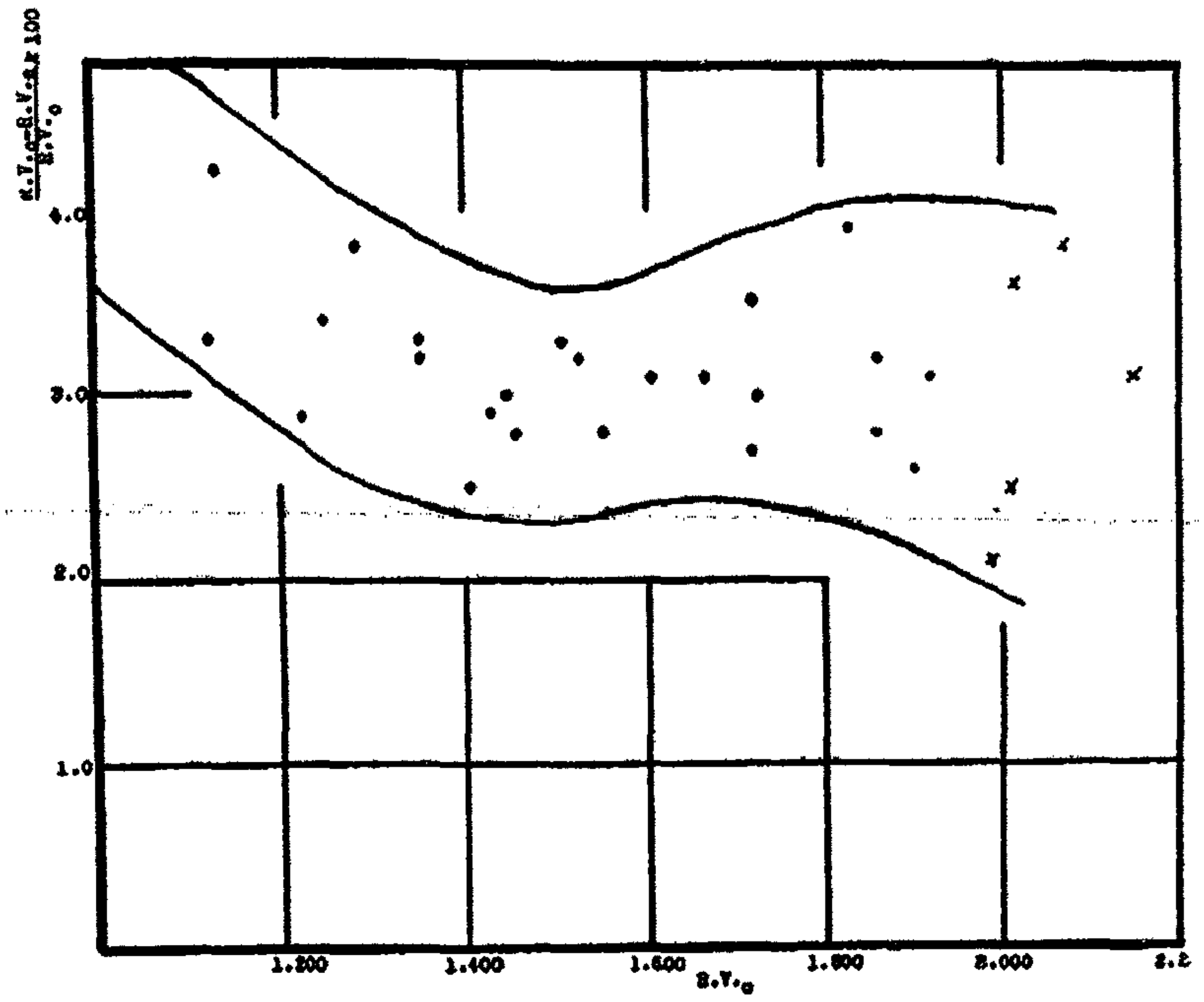

Fig. 7
Effect of Concentration on Radiosensitivity

Effect of Concentration

The methods previously described of changing the viscosity of 0.4% gelatine sols have changed the colloidal state of a given quantity of gelatine. A series of dilutions of the same sol differ in the closeness of packing of the micelles, but probably do not differ in the colloidal structure of the micelles, unless the concentration of some of the dilutions is sufficiently great for incipient gelation. In order to study the effect of radiation on sols of different viscosity but of the same structure, the radiosensitivity of a series of dilutions of the same sol was determined. One percent sols were made up in 0.010 N HCl, and a series of dilutions was made from each sol, so that the final concentrations ranged from 0.1% to 1.0%. The pH range of these dilutions was 3.3 to 3.5. It was shown in a previous section that sols of the same concentration have approximately the same sensitivity over this range. Half of each sample was then irradiated. The results are shown in Fig. 7. The initial sols are represented thus (x); the diluted sols are represented thus (.). The variation between the diluted sols is less than that between the initial sols. This series is entirely different from the preceding ones in that the more dilute and less viscous sols show a percent reduction in viscosity following irradiation as great as, or greater than, the percent reduction in the viscosity of the more concentrated sols.

Discussion

It appears from this work that X-rays reduce the viscosity of gelatine by reducing the swelling of the colloidal micelles. The more swollen are the micelles at the time of irradiation, the greater is the reduction in swelling brought about by the irradiation. When the degree of swelling of the micelles is reduced before irradiation, then the further reduction brought about by irradiation is slight. This is true whether the reduction in swelling is brought about by a shift of the gelatine from the α to the β form, by a change in the Donnan equilibrium conditions, or, qualitatively at least, by the effect of radiation itself. Further confirmation of the theory that the effect of radiation is on the swelling of the micelles is given by the fact that, when a sol is so diluted that the viscosity but not the structure is changed, the percent reduction in viscosity due to irradiation remains the same for different dilutions.

The evidence in the present paper is not sufficient to show that the degree of swelling of the micelles at the time of irradiation is the only property which determines the effect of irradiation. Other factors probably modify the reaction, and, in particular, the effect of X-rays on alkaline sols deserves further study.

Summary

The viscosity of dilute gelatine sols is decreased by heavy doses of X-rays.

When the viscosity of a given gelatine sol is reduced by heat, by pH change, or by the addition of salts, the percent reduction in viscosity due to subsequent irradiation is decreased.

When the viscosity of a given gelatine sol is reduced by ageing or by irradiation, the percent reduction in viscosity due to subsequent irradiation is decreased, but in a manner too irregular for quantitative interpretation.

When the viscosity of a given gelatine sol is reduced by dilution, the percent reduction in viscosity due to subsequent irradiation is not changed.

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DIELECTRIC CONSTANT OF ETHYL ALCOHOL VAPOR AND POSSIBLE EFFECT OF CONDUCTIVITY*

BY H. L. KNOWLES**

Abstract

The usual heterodyne beat method was used for determining the dielectric constant of ethyl alcohol vapor. Parts of the apparatus are described briefly and the method of calibrating the series condenser is discussed. Dielectric data were taken at a number of different temperatures over complete ranges of pressure. Except in the vicinity of the saturation pressure, $3(K - 1)/(K + 2)$ was found to vary linearly with p′, the ideal vapor pressure. Near saturation the slopes of the dielectric constant versus pressure curves increased quite markedly. The magnitude of this deviation was found to vary considerably with the solid insulators used in the test condenser. The value of the electric moment as determined from the slopes of the lower parts of the dielectric constant versus pressure curves is $1.68_9 \times 10^{-18}$. This value agrees closely with Miles' value of 1.69_6, and seems definitely to rule out Sänger's value of 1.11.

Complete data were taken of the direct current resistance of the test condenser at the various temperatures and pressures. The resistance was found to decrease rapidly near the saturation vapor pressure. Theoretically, this lowered leakage resistance is shown to be insufficient to account directly for the abnormally high dielectric constant values near saturation.

Introduction

The validity of the Debye equation has been tested for a large number of liquids and gases, and for a few vapors. In particular, measurements on ethyl alcohol vapor have been made by Bädeker,[1] Sänger,[2] and Miles.[3] Debye[4] has also made a calculation of the electric moment of the vapor molecule from refractive index data. Of these, the most recent and reliable data are those obtained by Miles.

Since the number of molecules present per unit volume of the vapor dielectric is proportional to the ideal pressure, Debye's equation in the simplified form may be written[5]

$$3\frac{K-1}{K+2}\frac{RT^2}{p'} = AT + B$$

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where K is the dielectric constant, R the gas constant per mol, T the absolute temperature, and A and B the Debye constants. p′ is the ideal pressure obtained from the approximate van der Waals' equation and is given by

$$p' = p\left\{1 + \frac{p}{RT}\left(\frac{a}{RT} - b\right)\right\}$$

From Debye's equation it is seen that at a constant temperature $3(K - 1)/(K + 2)$ should vary linearly with p′. Furthermore, if the quantity $3(K - 1)/(K + 2)$ is plotted against p′ for various temperatures, the slopes of the resulting straight lines multiplied by RT^2 give values of AT + B for various temperatures. By plotting these values of AT + B against T, a straight line of slope A and intercept B should be obtained. From B, the electric moment of the molecule may be calculated.

Since no complete data on ethyl alcohol vapor have been obtained, it was considered worth while to study the variation of the dielectric constant with pressure at a number of different temperatures. The value of the electric moment calculated from such data should be the most reliable so far obtained. That the relation between $3(K - 1)/(K + 2)$ and p′ might not be entirely linear was indicated by work by Zahn[6] and Wolf[7] on water vapor and by Maske[8] on benzophenone. They found the slopes of the lines increased quite markedly at some "critical" pressure. Zahn and Maske attributed this anomalous effect to the adsorption of the vapor on the condenser plates, while Wolf attributed it to the increased conductivity of the test condenser due to adsorbed vapor on the solid insulators. In view of the findings of Wolf, it was thought advisable to make complete conductivity measurements along with the dielectric constant measurements.

Experimental Method

The dielectric constant measurements were made by the usual heterodyne beat method.[9] Since in the case of vapors the capacity changes to be measured may be as small as a few hundredths micro-micro-farads, it was necessary to place a smaller condenser in series with the variable precision condenser. This series arrangement was placed in parallel with the test condenser (Fig. 1). The capacity of the series condenser C_s was determined by placing a standard variable precision condenser C^1_p in parallel with the test condenser. Known variations were made in C^1_p and then the original capacity of the circuit restored by making equivalent changes in C_p. By properly setting the variable air condenser C_1, it was possible to vary C^1_p by small consecutive steps until the entire scale of C_p had been covered. Several hundred different capacity changes were thus measured. From these data a curve was plotted of known capacity changes of C^1_p against corresponding capacities of C_p. Known sets of values of $\triangle C_p$, $\triangle C^1_p$, and C_p were taken from the curve and the

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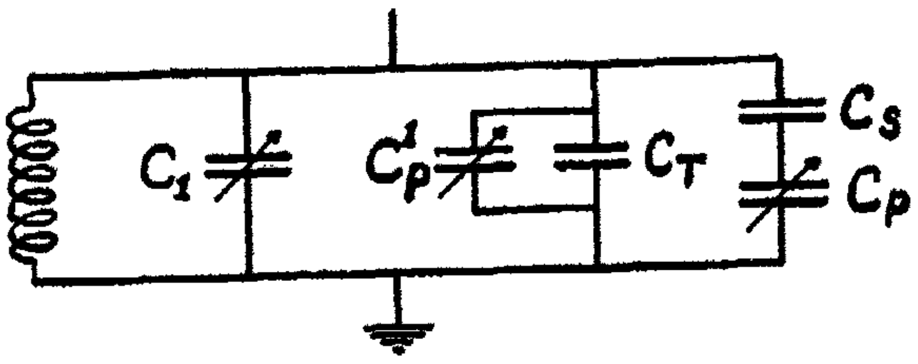


FIG. 1

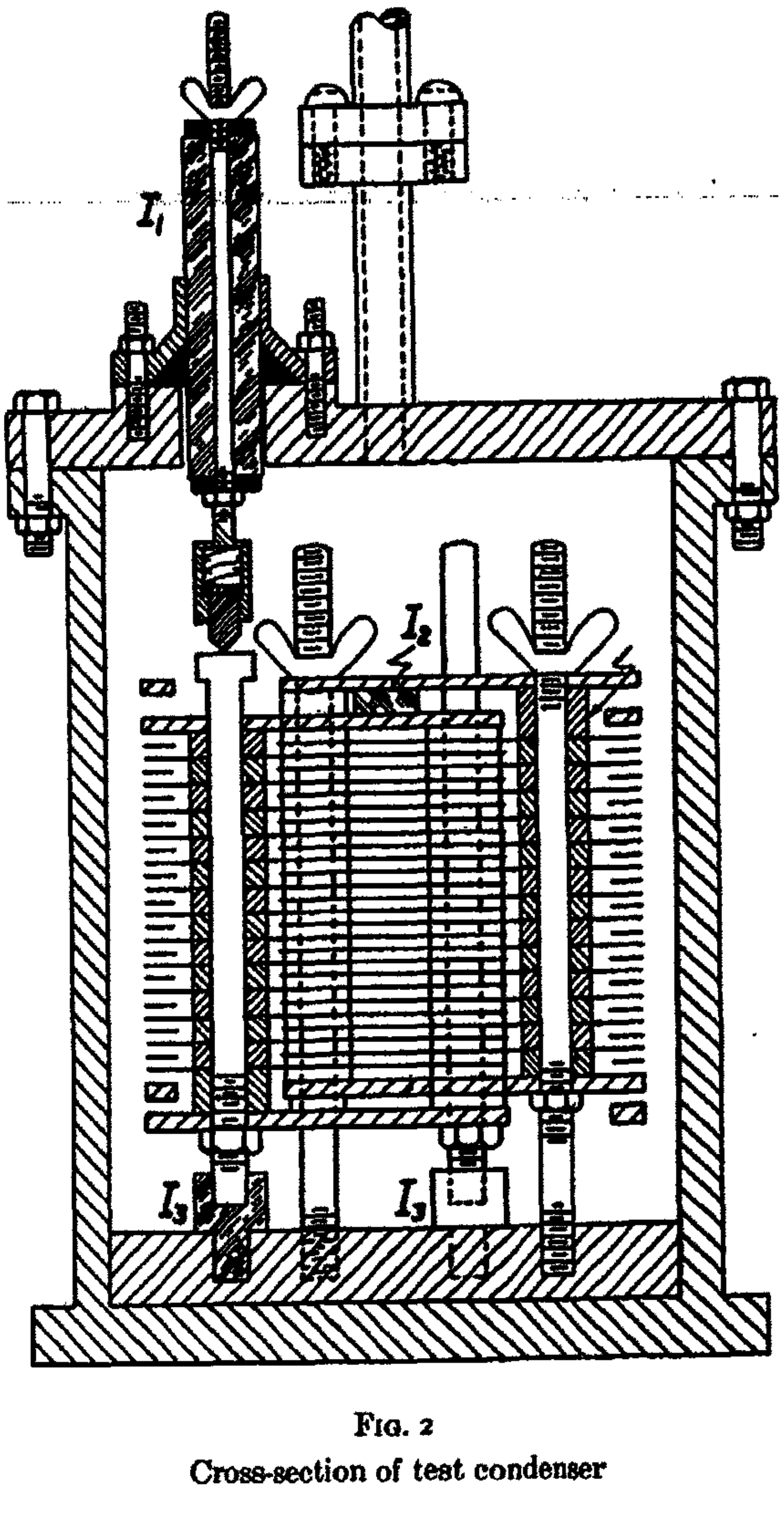
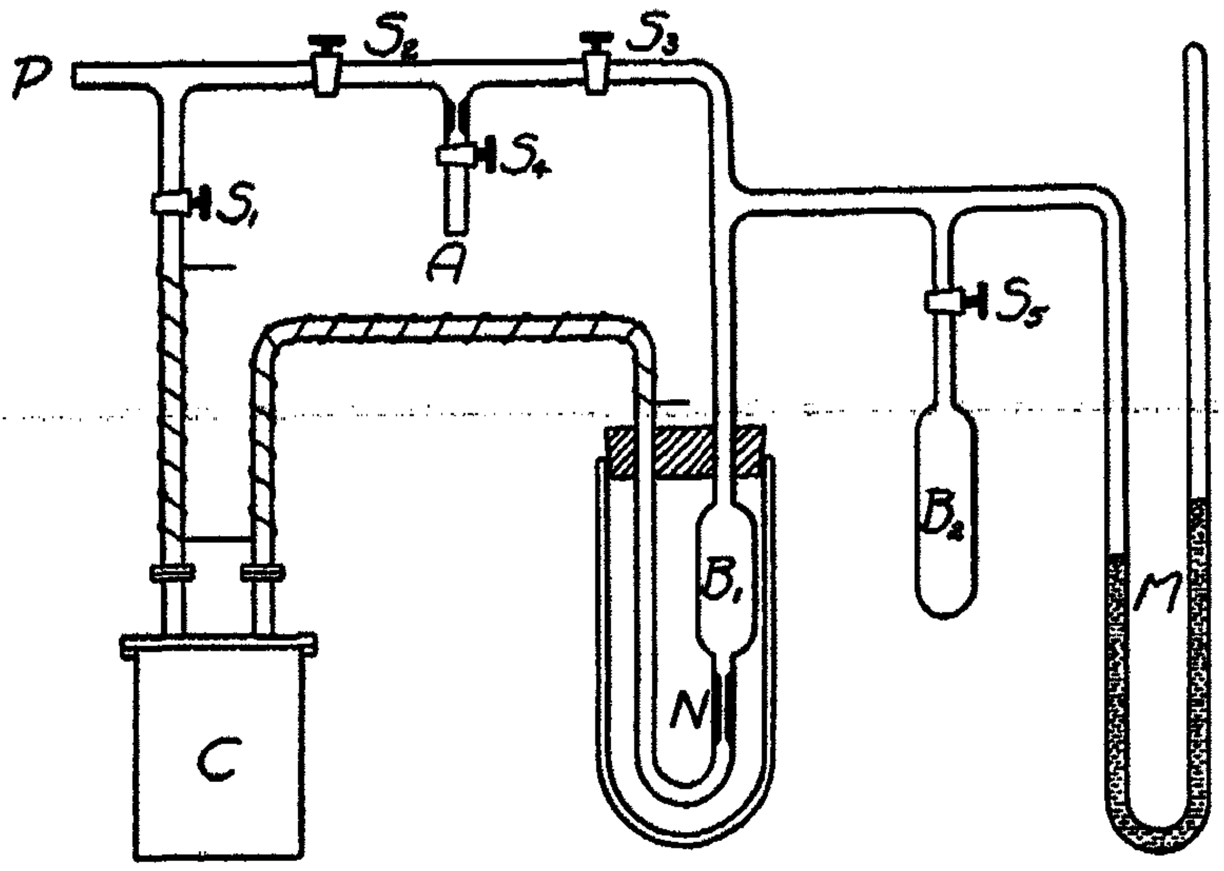


FIG. 2
Cross-section of test condenser

corresponding values of C_s calculated. It is interesting to note that the average value of C_s thus obtained differed by over 10% from that obtained by direct measurement. The difference was due to the fact that when measured directly, one terminal of C_s was grounded, while in the method used neither terminal was grounded. Since in use neither terminal of C_s was grounded, this method of calibration was necessary.

The precision condensers were type 222, General Radio condensers, and were calibrated by measuring the capacity change for every hundred divisions in terms of a fixed interval on another similar precision condenser placed in parallel. The worm gear was checked in a similar manner. Capacity changes as measured on C_p should be in error by less than .06 m.m.f.



VAPOR SYSTEM

FIG. 3

The test condenser (Fig. 2) was constructed of ¼″ brass tubing with ⅜″ bottom and lid. All joints were silver soldered. The two sets of circular brass plates were supported from a heavy brass disc set in the bottom of the container. The plates were spaced by means of brass washers. The insulated set of plates was held rigid by means of the three solid insulators I_3 and the one insulator I_2. The lid and insulator I_1 were made airtight by the use of lead gaskets. This construction allowed the changing of the plate spacing, the plate material, and the material of the solid insulators. The capacity of the test condenser was about 940 m.m.f. The distributed capacity of the test condenser was obtained by measuring the capacity of the leads with the circuit open at the inner end of I_1. I_2 was the only solid insulator in the electric field inside of the condenser, and the unchanged capacity due to it was calculated from geometric considerations. The test condenser was immersed in a thermally insulated constant temperature oil bath. Temperatures were measured with a platinum resistance thermometer.

The vapor system (Fig. 3) was similar to the one used by Miles.[3] It had the advantage of two exhausts in the test condenser, one exhausting on each side of the liquid ethyl alcohol contained in the U-tube at B_1. Any air which might enter the test condenser around the U-tube, due to too violent boiling of the alcohol in the heated arm of the U, could be immediately removed by evacuation through the cock S_1. The measurement of the change in the capacity of the test condenser caused by evacuation was made immediately after the reading at any given pressure was taken. This tended further to eliminate any error which might have been introduced by any gradual changes in the electric circuits. The bulb B_1 and U-tube were immersed in a dry ice bath which maintained a temperature between −70°C and −80°C. Both an organic and an inorganic stopcock lubricant were used, and no effect of either was detected in the results.

The resistance of the test condenser was measured by charging it to a known potential and allowing it to discharge through its leakage resistance, the change in potential being determined with an electroscope.

The ethyl alcohol was prepared from the commercially pure product. It was carefully dried by reflux distillation for twenty-four hours over calcium oxide and then distilled off, the middle fraction only being used. All samples of alcohol used were tested for the presence of water with anhydrous copper sulphate.

Data and Results

The first set of measurements (Table I) was taken at a temperature of 24.55°C, which was the lowest temperature at which the oil bath could be maintained conveniently without some special means of cooling. Data were taken for pressures varying from 2 mm to near saturation, which in this case was about 5.8 cm of Hg. The solid insulators were of Pyrex. The values of p and p′, and of $(K - 1)$ and $3(K - 1)/(K + 2)$ are essentially the same at the low pressures used here. The curve (Fig. 4) of $3(K - 1)/(K + 2)$ plotted against p′ is a straight line from a pressure of 2 mm to within about 1 mm of saturation. The curves for 46.55°C, 58.90°C, and 74.72°C (Fig. 5) are also linear from pressures of a few millimeters to near saturation. However, near saturation, the slopes of the lines increase very abruptly. This occurs at a pressure about 1.5 cms of Hg. below saturation at 58.9°C, and about 2 cms below saturation at 74.7°C. These changes in slope appear to be similar to the ones found by Zahn and Wolf in the case of water vapor, except that there is no marked tendency for this effect to disappear as the temperature is raised. The remaining data in Table I were taken at temperatures above the normal boiling point of ethyl alcohol, so saturation pressures were not reached. As would be expected, the curves were linear over their entire extent. The slopes of the lines corresponding to temperatures of 137.8°C and 170.5°C were determined by taking the average of a number of readings taken at approximately one pressure.

The resistance data for the test condenser with Pyrex insulators are shown in Fig. 6. The resistance is seen to decrease quite markedly as the saturation

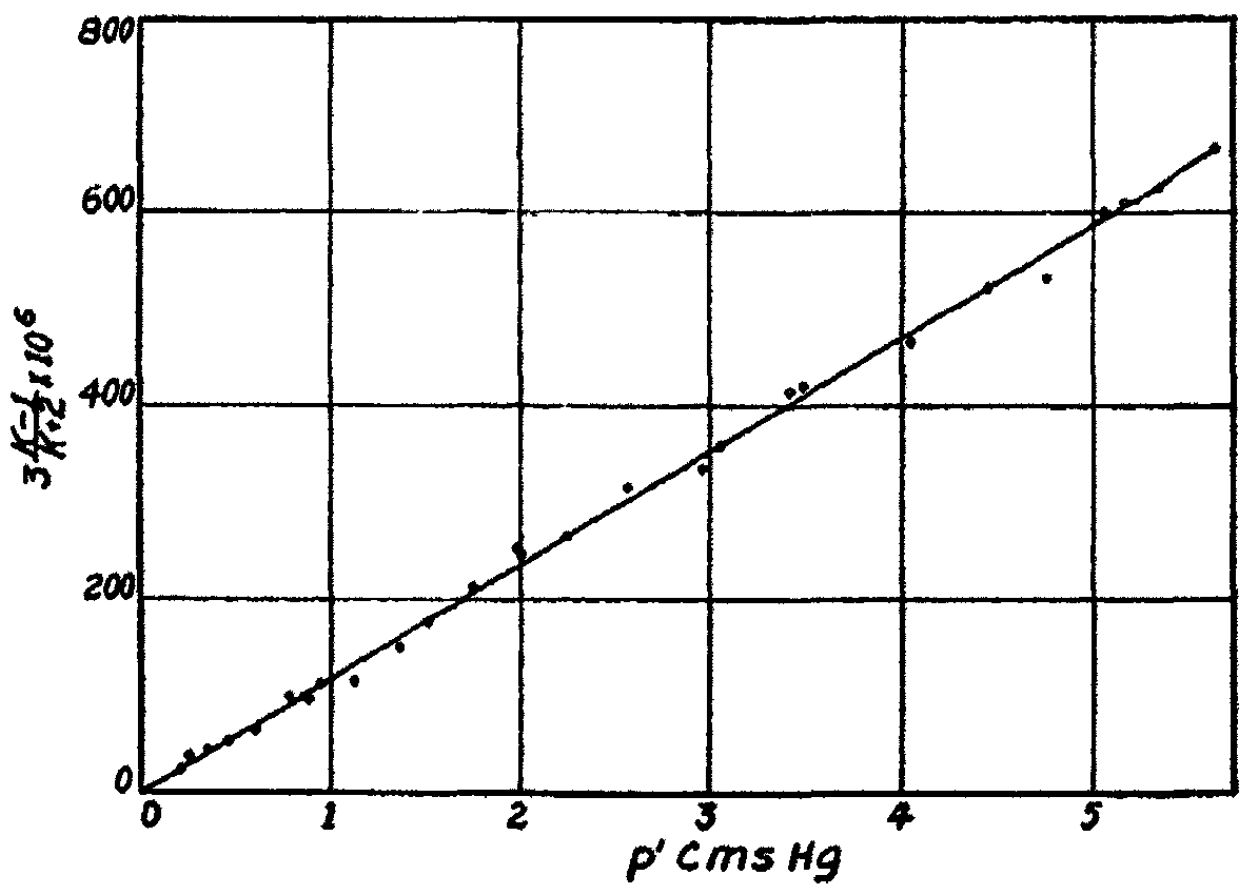


FIG. 4

The variation of polarization with the corrected pressure, p', for ethyl alcohol vapor at a temperature of 24.55°C.

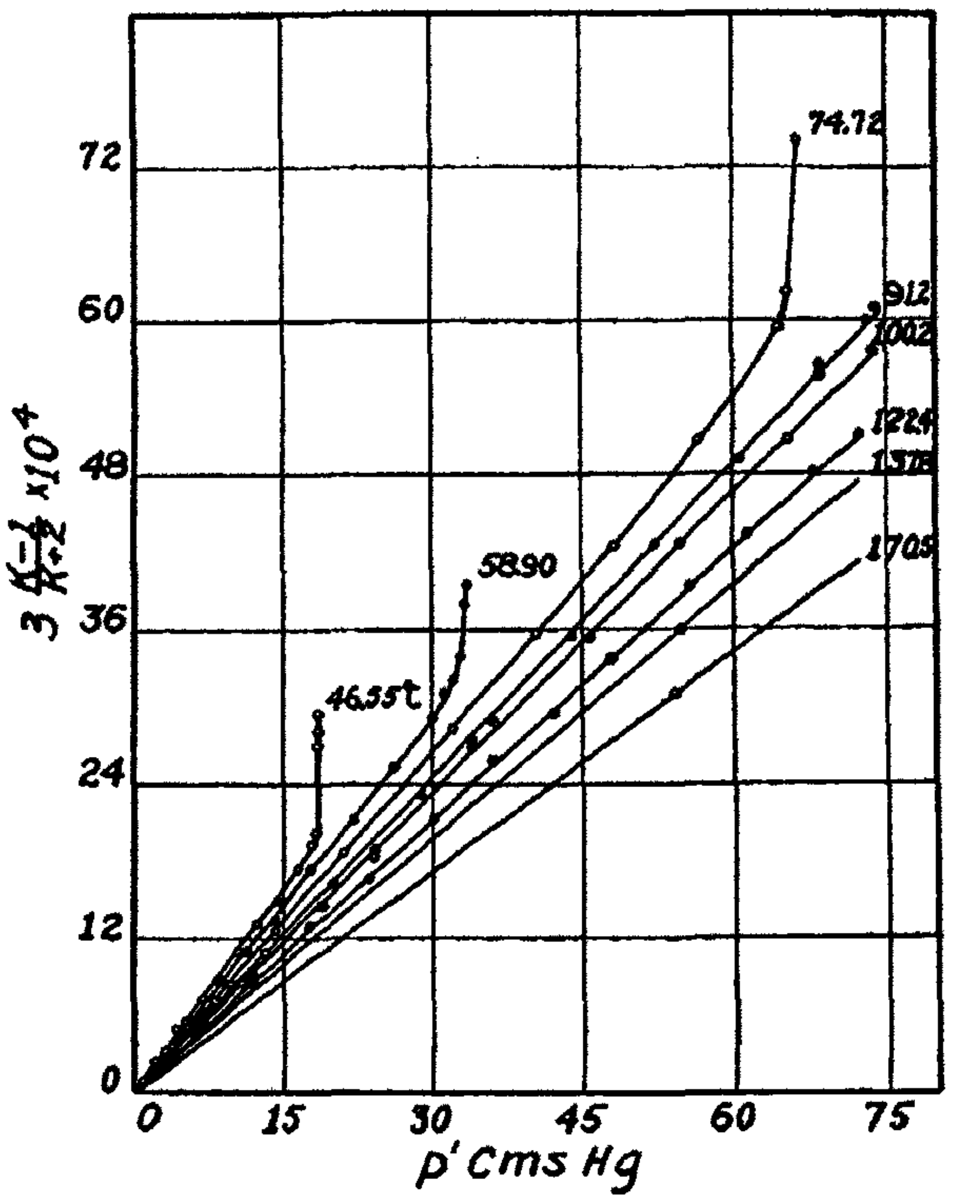


FIG. 5

The variation of polarization with the corrected pressure, p', for ethyl alcohol vapor, using Pyrex insulators. Temperatures range from 46.55°C to 170.5°C.

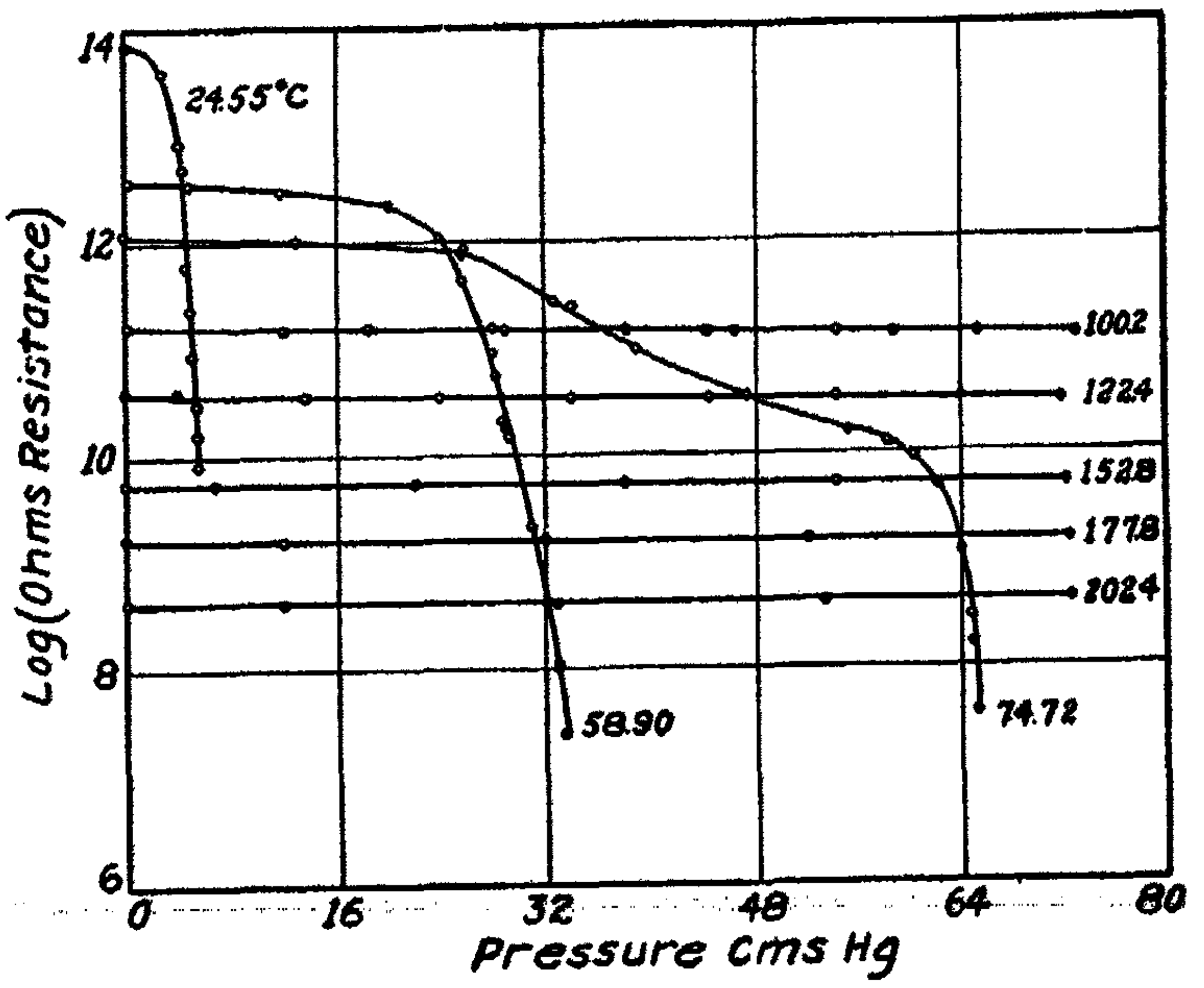


Fig. 6

The dependence of test condenser resistance upon vapor pressure at various temperatures, using Pyrex insulators.

TABLE I*

Summary of Dielectric Constant Data

t°C	T°K	$\frac{(K-1)\times 10^6}{p}$	$3\frac{K-1}{K+2}\times\frac{10^6}{p'}$	AT+B
** 24.55	297.5	117.3	117.2	64,990
46.55	319.5	103.0	102.6	65,650
58.90	381.9	96.0	95.5	65,960
74.72	347.7	88.5	87.9	66,600
91.20	364.2	82.2	81.4	67,670
100.2	373.2	78.7	77.9	68,000
122.4	395.4	70.6	70.0	68,570
137.8	410.8	65.9	65.6	69,640
170.5	443.5	57.6	57.3	70,580
*** 58.90	381.9	96.0	95.5	65,960
74.72	347.7	88.5	87.9	66,600
177.1	450.1	56.1	55.8	70,920

* p and p′ in cms of Hg.

** Data taken with Pyrex insulators.

*** Data taken with quartz insulators.

pressure is approached. At higher temperatures where the pressures are below saturation, the relation between the logarithm of the resistance and the vapor pressure is practically a linear one.

The Pyrex insulators in the test condenser were next replaced by fused quartz, and dielectric constant data were taken for three temperatures. The curves are shown in Fig. 7. The marked change in slope found previously with the Pyrex is nearly absent. This can be distinctly seen in Fig. 8 where data obtained with both insulators at the same temperature are plotted on a single curve. The resistance curves are essentially of the same form as found for the Pyrex. In the vicinity of the saturation pressure the resistance in the case of the quartz was higher by a factor of about ten.

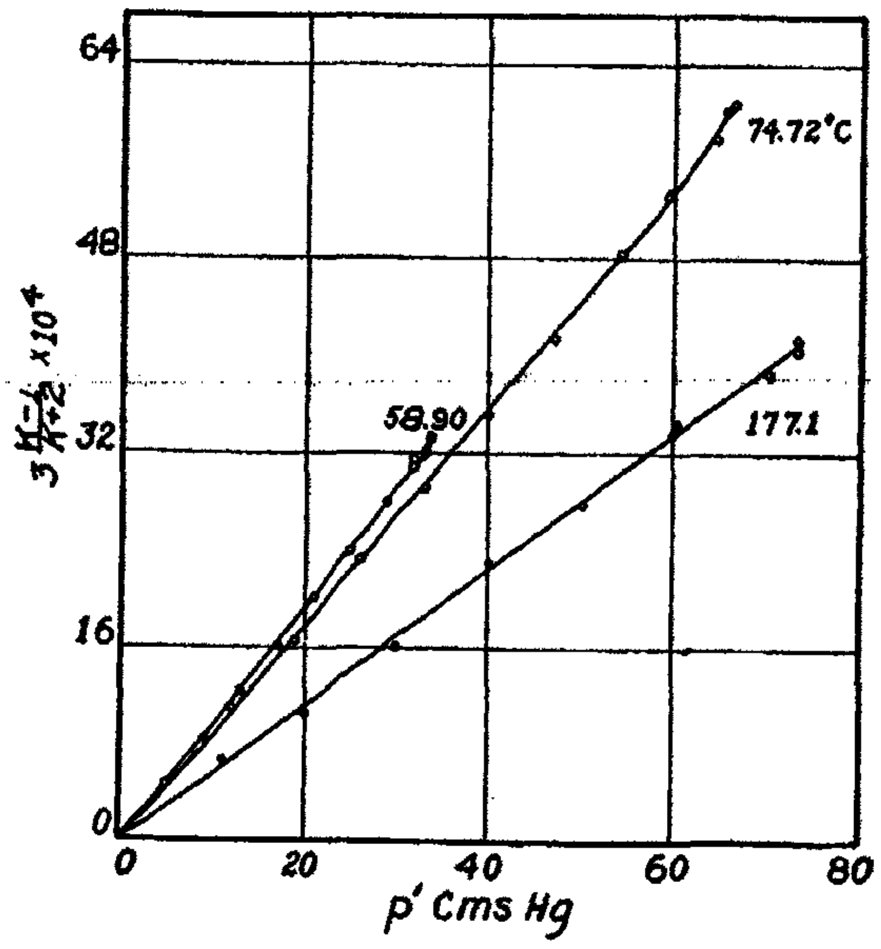


Fig. 7
Variation of polarization with the pressure, p', at various temperatures, using quartz insulators.

In order to obtain the value of the electric moment of the ethyl alcohol molecule, a curve was plotted of $3(K - 1).RT^2/(K + 2)p'$ against the absolute temperature. The slopes of the lower linear parts of the dielectric constant versus pressure curves were multiplied by RT^2 to obtain $AT + B$. These values are tabulated in Table I and the curve is shown in Fig. 9. The maximum deviation of any of the twelve points from the Debye straight line is less than .5%. The value of the intercept as calculated by the method of least squares was 52,650 and the value of the electric moment was $1.68_6 \times 10^{-18}$. This value compares quite favorably with Miles'[3] value of 1.69_6 and rules out definitely Sänger's value of 1.11.

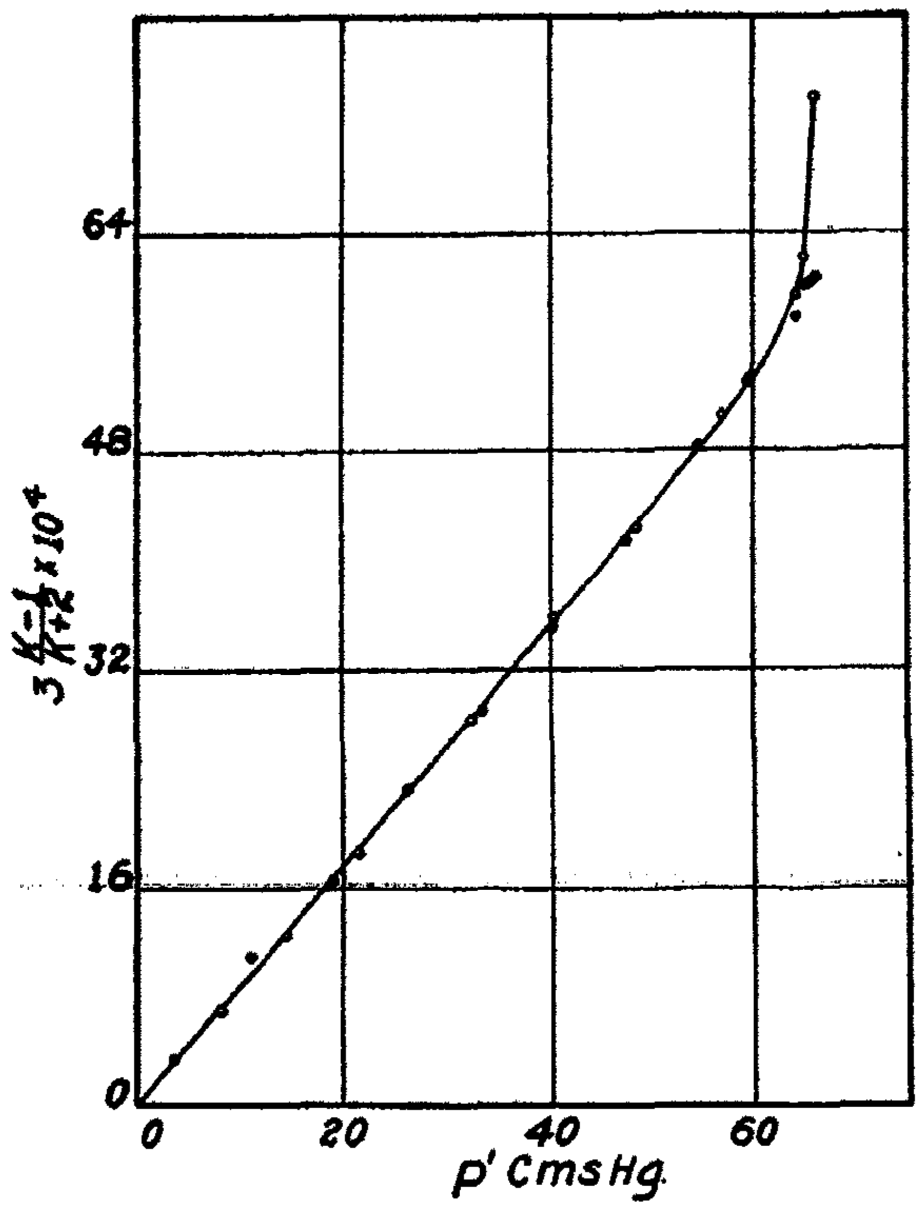


FIG. 8

Variation of polarization with the pressure, p', at 74.72°C. Data obtained with quartz insulators are shown by the solid dots, and data obtained with Pyrex insulators by the circles.

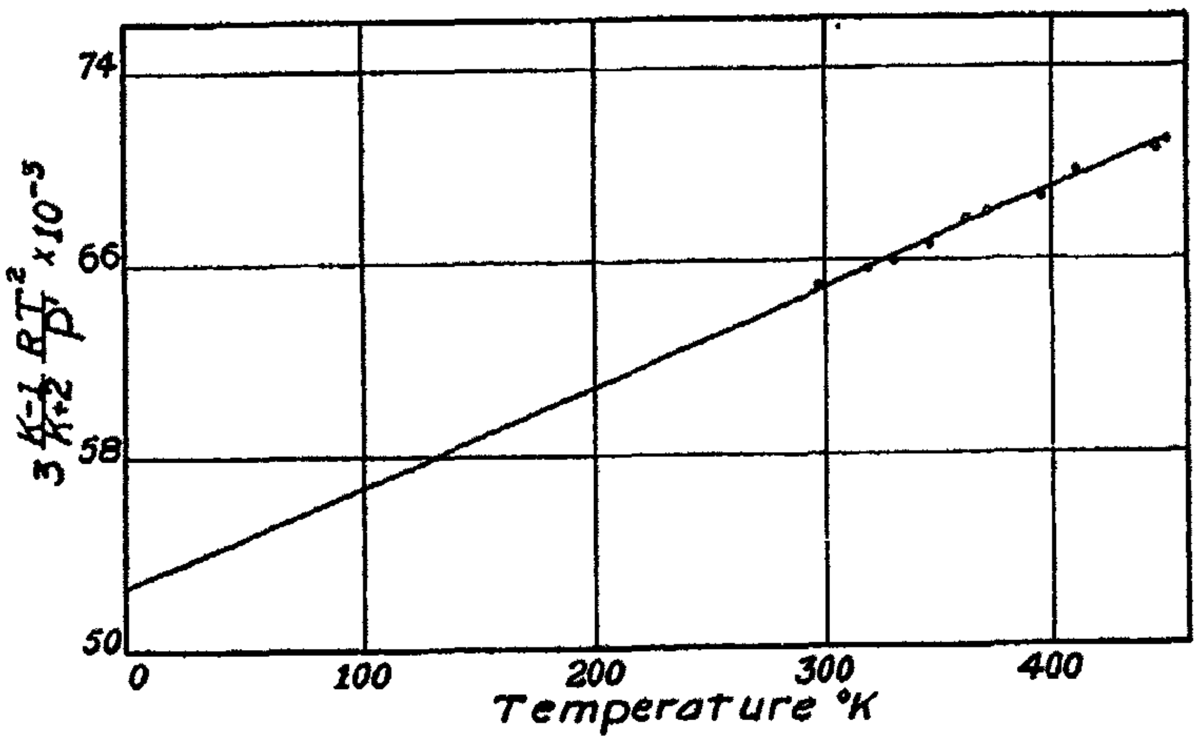


FIG. 9

Debye line for ethyl alcohol vapor.

Possible Effect of Conductivity

It was desired to determine both experimentally and theoretically if the lowered leakage resistance of the test condenser near the saturation vapor pressure could account for the observed deviations in the dielectric constant curves. To determine this theoretically, the effect of the leakage resistance on the output circuit of the oscillator was considered. The output circuit may be considered as containing in place of a triode an alternator of generated e.m.f. E and resistance R_p connected in series with a parallel combination of three branches. One branch contains an inductance coil of resistance R_L and reactance X_L, the second branch is the condenser leakage resistance R_c and the third branch contains the condenser having a reactance X_c. By applying Kirchoff's laws, an expression may be obtained for the current I_L through the inductive branch in terms of the constants of the circuit and the e.m.f. E. If the grid current be neglected, E may now be expressed in terms of the amplification factor of the tube, the mutual inductance between the grid and plate circuit inductance coils, and the current I_L through the coil in the plate circuit. By combining these two equations for the current I_L through the inductive branch, both E and I_L are eliminated. A resultant expression containing only constants of the circuit may be obtained by equating the imaginary parts in the equation. When solved for the capacity C, this expression becomes

$$C = \left\{1 + R_L\left(\frac{1}{R_c} + \frac{1}{R_p}\right)\right\}\frac{1}{2\pi f X_L}$$

Since the frequency of the oscillator is maintained constant at about 500 kilocycles, and X_L and R_L do not change, changes in R_c or R_p must be compensated for by changes in the capacity C. The values of R_p and R_L are approximately 2×10^4 and 10 ohms, respectively, and X_L is 310 ohms. Then to maintain a constant frequency, the change in capacity occasioned by the decrease in R_c from 10^{13} to 10^8 ohms, is 10^{-4} m.m.f. This change is entirely too small to account for the observed dielectric constant deviations, since at 58.90°C at a vapor pressure corresponding to a test condenser resistance of 10^8 ohms, a capacity change of 3300×10^{-4} m.m.f. is necessary. Furthermore, this change in capacity is not only too small, but in the wrong direction. When the test condenser is evacuated, its capacity is a minimum and the capacity of the parallel precision condenser (Fig. 1) is a maximum. R_c is also a maximum. The introduction of the vapor increases the test condenser capacity on account of its dielectric effect and, consequently, the precision condenser capacity must be decreased to maintain a constant frequency. However, the introduction of the vapor causes a decrease in R_c which necessitates a slight increase in the total capacity to maintain a constant frequency, as seen above. Therefore, the precision condenser capacity change will not be as large as it would have been if the resistance had not been lowered. Consequently, the calculated dielectric constant would be too small.

In the above equation it is seen, however, that any change in R_p caused by a change in R_c would be quite noticeable, due to the fact that R_p^{-1} is greater than R_c^{-1} by a factor of 10^4. In order to determine how effective the changes in R_c might be in changing R_p, an expression was obtained for the total impedance of the three parallel branches. X_c was eliminated from this expression by means of the above equation for C. The resultant expression for the total impedance is

$$Z = \frac{R_cX_L^2(X_L^2 + R_LR_c + R_L^2) - J\,R_LR_c^2X_L[R_L(1 + R_LB) + X_L^2B]}{R_cR_L[R_LR_c(1 + R_LB)^2 + 2X_L^2] + (R_LR_cX_LB)^2 + X_L^2(R_L^2 + X_L^2)}$$

where $B = 1/R_c + 1/R_p$.

While it is not possible to calculate R_L exactly, its value is probably between 5 and 10 ohms. Taking the value of R_L as 10 ohms and that of X_L as 310 ohms, the effect on Z of lowering R_c to 10^8 ohms is practically negligible, being 1 part in 10,000. The fractional change in phase angle is entirely negligible. If R_L is taken as 5 ohms, the fractional change in Z introduced is 1 part in 7000 and the phase angle is changed by 1 part in 8000. Certainly any change in R_p due to such a small change in Z would be entirely negligible. This conclusion is in agreement with experimental data on the type of tube used, which show that a change of 1 ohm in load resistance causes a change of about .5 ohms in plate resistance at the plate voltage used. This change in R_p, together with the corresponding change in R_c cause a change in capacity of 1.1×10^{-4} m.m.f., as calculated from the preceding expression for the capacity C.. This differs very little from the previous value obtained by neglecting changes in R_p.

In deriving the expression for the capacity C, the input capacity of the triode was neglected. The five-mesh network including the grid-plate and grid-filament capacities cannot be solved readily as in the previous case, as the equations become too long and cumbersome. It seems doubtful though that the above results would be greatly affected by considering the tube capacity, since the change in effective input capacity caused by the changes in R_c and R_p is only 10^{-3} m.m.f.

A direct measurement of the effect of a leakage resistance is difficult to make, since the change in the actual distributed capacity of the system caused by switching in a resistance is quite likely to mask entirely the leakage effect. For this reason, there may be some question about such measurements as were made by Wolf.[7] In the present case the effects of a number of different, though geometrically duplicate, resistances were measured. These resistances were introduced singly in parallel with the evacuated test condenser. While the distributed capacity change introduced was by no means negligible, it should have been practically the same for the different resistances. The resistances used varied from 10^4 to 10^7 ohms. Between 5×10^5 and 10^7 ohms, the effective capacity of the circuit was increased by from 0 to .2 m.m.f. Between 5×10^5 and 10^4 ohms, the effective capacity was decreased by the introduction of the resistance by from 0 to 9 m.m.f. The increase in effective capacity at high resistance is doubtless due to the actual capacity introduced by the resistance used. The effect of the resistance is apparently to decrease the effective capacity of the circuit, the effect being much more pronounced at low resistance. At 10^7 ohms, the increase in capacity is too small to account for the observed dielectric constant deviations, even though it be assumed (which is certainly not the case) that the capacity increase is due to the resistance effect alone.

The author is fully convinced from his observations that the direct current leakage resistance of the test condenser cannot account quantitatively for the observed deviation from the Debye straight line near saturation. On the other hand, he is fully convinced that there exists a very intimate connection between this leakage resistance and the deviation. The fact that the resistance curves show marked breaks at the same vapor pressures as do the dielectric curves strongly indicates a close connection. If the deviations in dielectric data are to be accounted for directly and quantitatively by the leakage resistance of the test condenser, then the author feels that the magnitude of the leakage resistance at high frequency and the effect of this upon the condenser capacity must be distinctly different from that observed with a direct potential.

Summary and Conclusions

A method was used for calibrating the series condenser directly as it was to be used in series with the precision condenser. This eliminated the error present in the common method of measurement in which one terminal of the series condenser is grounded during the calibration, but not grounded when in use. The error thus eliminated was found experimentally to be quite appreciable, as much as 20% in (K − 1) in some cases.

The vapor system was so arranged that the dielectric measurements were relatively independent of any gradual variations in the electrical system, since the readings for any given pressure were all taken within two minutes once equilibrium had been reached. Any air admitted into the test condenser either by a leak or around through the U-tube due to too violent boiling at the heated surface was readily removed after each reading since the test condenser was completely evacuated directly.

The relation between $3\,(K-1)/(K+2)$ and the corrected pressure p' was found to be linear at all temperatures, except near the saturation vapor pressure.

The direct current resistance of the test condenser filled with vapor was found to decrease very rapidly as the saturation pressure was approached. The resistance in the case of quartz was found to be slightly higher than for Pyrex.

The breaks in the dielectric constant curves cannot be explained quantitatively by calculating the effect of the leakage resistance upon the effective capacity of the oscillatory circuit. The calculated effect is much too small, and in the wrong direction. However, since the dielectric constant and resistance curves have breaks at approximately the same pressures, it seems quite probable that the two effects are quite closely related.

Direct measurements upon the effect of a leakage resistance seem to show that the effect of the resistance is entirely too small and in the wrong direction to account for the observed deviations in the dielectric constant curves.

The observed points of $3(K-1)RT^2/(K+2)p'$ as determined from the slopes of the pressure curves, when plotted against the absolute temperature, fall closely on the Debye straight line. There is no marked deviation found at the lower temperatures, as was found by Miles[7] at a temperature of 351°K, although four readings were taken at temperatures lower than this. Thus Miles' assumption of association seems to have little foundation. Also, Sänger's[6] curve which showed a marked deviation from the Debye straight line is at variance with the present results. In the present work no one of the twelve points obtained falls as much as .5% from the straight line drawn through the points.

In conclusion, the writer wishes to thank Dr. J. D. Stranathan, under whose direction this problem was undertaken, for his continued assistance throughout the work, and Dr. H. H. Germond, for his valuable suggestions.

THE BEHAVIOR OF METALLIC SOAPS WITH ORGANIC SOLVENTS

BY JAMES W. McBAIN AND WINIFRED L. McCLATCHIE

One of us[1] pointed out that the behavior of soaps towards aqueous solution demonstrated the thermodynamic stability of the colloidal state for certain cases as compared with crystalloidal and crystalline states. This view has apparently been accepted as regards many sols. However, it has been questioned as applicable to jellies. It is, therefore, of interest to see in how far a spontaneous formation of jellies from crystalline material and pure solvents can occur. Such instances are encountered amongst soaps in contact with organic solvents. Within a very narrow range of temperature and concentration this has been reported for sodium oleate and water.[2]

Again, very little work has been done on jellies of known chemical formula like soaps and in non-ionizing media where ionic and Donnan equilibria are eliminated and where the results gain significance from the simplicity of the conditions.

To create a jelly, molecules must organize. In a stable sol this is done by the spontaneous formation of colloidal particles, each consisting of an orderly array of molecules whose relative positions are a result of the characteristic properties of the different groups in each molecule. For a jelly something more is required; some structure must be built up from the separate micelles.[3] For supermolecules of a chain-like nature juxtaposition might suffice. In all cases there must be an affinity between the solvent and some grouping of the molecule exposed in the micelle. Swelling will be due to two separate causes. First, direct combination, sorption, or polarization of molecules, or clusters or strings of molecules of solvent with the exposed groupings. Second, through the penetration of free molecules of solvent between the interlacing structures to release strains and tensions in the structure, because close packing will not in general accord with the undistorted shape and arrangement of molecules and micelles. The first factor in swelling will correspond to the thermodynamic properties represented by the vapor pressure of the solvent in the system. The second, when present, will give rise to an additional swelling pressure of as purely mechanical origin as the familiar spontaneous refilling of a rubber tube with air after the tube has been squeezed, the pressure released, and the ends opened to the atmosphere. This second process is well demonstrated by the observations of Stamberger and Blow[4] on the swelling of vulcanized and unvulcanized rubber. Swelling

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[1] J. W. McBain: Colloid Symposium Monograph (Cambridge, 1926), 4, 1 (1926).

[2] M. E. Laing and J. W. McBain: J. Chem. Soc., 117, 1506 (1920).

[3] Compare J. W. McBain: J. Phys. Chem., 30, 239 (1926); Trans. Faraday Soc., 20, 22 (1924).

[4] P. Stamberger and C. M. Blow: Nature, 124, 13 (1929); Rubber Chem. Tech., 2, 591 (1929).

pressure will correspond to vapour pressure only when there is no such structural factor to consider. The thermodynamic equation assumes that all of the pressure applied to the jelly is effectively transmitted to the solvent, for it is the pressure on the solvent that is given by the equation. For this reason calculated values for swelling pressures may be expected to be less than experimental values.

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The first step when a crystal is placed in contact with a solution is the separation of the molecules by molecules of solvent. If this process is complete, they pass into solution. But concurrently micelles may be organized. If they are largely separated they pass into solution as a sol. If they are not sufficiently separated they merely form a swollen mass below the liquid. If the packing of the molecules in the crystal is sufficiently dense and the constitution such that lyophilic groups are not exposed to the solvent, the crystal will appear nearly insoluble and it will not swell.

It is quite otherwise with the solid produced after the crystal has been once brought into solution, as for example by heating, and then dried. The dried mass now retains something of the organization of a jelly and it must swell when placed in contact with cold solvent. The first stage in swelling must then occur, due to a forcing apart of the micellar units existing in the dried jelly through the affinity between solvent and lyophilic groups. This, owing to the minute dimensions of the structure, could produce a very appreciable increase in volume. The question as to whether or not swelling will be followed by the micelles passing into solution as a sol depends upon the balance of forces previously mentioned between the cohesive groups for each other and for solvent. A decisive factor is concentration, a certain minimum concentration of micelles being required to form a coherent jelly or gel. For example, this is 12 per cent for aluminium dipalmitate in dry xylene to form a clear firm jelly. Another decisive factor is temperature. With our systems the higher the temperature, the more complete the interaction between solvent and solute. Thus at sufficiently low temperatures the interaction may be so suppressed that there is little or no swelling, whereas at sufficiently high temperatures a fully formed jelly will disintegrate to separate micelles and these will tend ultimately to separate into single molecules.

Instances of each of the kinds of behavior outlined in the foregoing paragraph are to be found in the case of soaps and organic solvents.

It will be noted that the comprehensive scheme outlined above includes agreement with the views put forward by Whitby[1] in 1926 on page 216 of his paper but not with those he presents on pages 218 and 219. He has made the assumption that all of the solvent imbibed by a swelling colloid is due to solvation, quoting examples of the taking up during swelling as much as 20-40 times more solvent than the original weight of solid. It is indicated above how and why only a small proportion of it need be so regarded. The slightest pressure or, in some of our cases, a slight lowering of temperature serves to liberate large portions of the imbibed solvent, showing how negligible must be the chemical affinity. Whitby is too much inclined to consider

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[1] G. S. Whitby: Colloid Symposium Monograph (Cambridge, 1926), 4, 216 (1926).

that McBain's point of view depends solely upon the results of sorption experiments, not weighing as well the arguments from the mechanical explanations and models of apparent viscosity.

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As regards the argument used by Whitby and others that no particles are visible in benzene solution of rubber when examined with the ultramicroscope, it may be pointed out that in 1925 McBain and Dr. H. Harris examined with the best ultramicroscopes then available all of the clear and transparent aqueous jellies which had been described in the literature up to that time, and they found that all jellies can be prepared so clear that they cannot be resolved in the ultramicroscope, just as in the case of very fine gold sols where only a Tyndall cone remains. This does not mean that in dilute jellies such substances as, for example, manganese arsenate and zinc arsenate are to be regarded as having combined with all the water present but rather that the degree of dispersion is exceedingly fine. Indeed, in many cases envisaged above, it might be molecular without the molecules losing their coherence with other molecules at portions of their surface. One need only recall in this connection the possibilities opened by the work of Sheppard, Nietz, Keenan, Devaux, Gorter, Grendel, Zocher, etc., who have shown that various colloids of high molecular or micellar weight such as proteins, rubber, etc. can spread as coherent films on surfaces of mercury or of water to such large areas that their average thickness is only a few Ångstrom units. Indeed, the term degree of dispersion as ordinarily used has lost most of its significance on account of the great rarity of completely independent primary particles. A sol or a jelly of ferric hydroxide can easily be made so clear that it is not resolved in the ultramicroscope and yet unable to pass through the pores of ordinary filter paper.

Enormous solvation is assumed by many writers in trying to explain why such colloids are not resolvable in the ultramicroscope by making the further assumption that the colloidal particles are thereby so diluted that their refractive index approaches that of the solvent itself. This hypothesis is forced and wholly unnecessary. Even gold particles whose interior is crystalline and whose refractive index differs ever so much more from that of water cannot be resolved in the ultramicroscope if they are less than about 40 Å in diameter.

Few seemed to have followed our argument, repeatedly put forward, that if a jelly can be prepared thus optically clear without losing any of its characteristic properties, the significant properties of the jelly must be due to the invisible particles. Even when the jelly, less carefully prepared, shows a number of resolvable particles, these do not constitute its structure and the fact that they may be more or less distant from each other possesses no particular meaning and does not disprove the conception of jelly structure as due to interlocking of the unresolved and unresolvable particles.

The present summary of observations made in 1929[1] is part of a search for a suitable pure chemical substance for quantitative study of jellies in

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[1] Miss W. L. McClatchie, Thesis for the degree of Master of Arts, Stanford University, December, 1929. A few months later M. H. Fischer and M. O. Hooker (Kolloid-Z., 51, 39 (1930)) published observations which supplement those given here.

non-aqueous solutions. It concerns twenty soaps with xylene, and for silver, sodium, and aluminium palmitates about fourteen other solvents.

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Preparation of Soaps

Silver palmitate was made by mixing a solution of silver nitrate in alcohol with excess of hot alcoholic solution of palmitic acid, washing the precipitate with 95 per cent alcohol and with ether. On ignition 29.7 and 29.5 per cent of silver (theoretical being 29.7 per cent) was obtained. Thorium palmitate was similarly prepared.

Most of the soaps were prepared by precipitation of sodium soaps from aqueous solution. The sodium and potassium soaps were especially made for us by Kahlbaum. We have pointed out elsewhere[1] that normal aluminium soaps such as tripalmitate do not exist but that if prepared in contact with aqueous solution the amount of combined fatty acid does not much exceed the monobasic compound, and even if prepared most carefully in anhydrous solvents with excess of fatty acid, there are not more than two equivalents of combined fatty acid in the molecule.

It is, of course, of direct significance in the wedge orientation theory of emulsions where the aluminium palmitate has been erroneously assumed to be a tribasic soap although the conditions are ideal for hydrolysis and abstraction of the fatty acid even had the tribasic soap been originally capable of existence.

Behavior towards Xylene

For a given soap the swelling increases with increase in temperature. At a given temperature the swelling of soaps with the same cation increases with increasing molecular weight and is greater for soaps of unsaturated than for soaps of saturated fatty acids. For different soaps of the same fatty acid there is a tendency towards increased swelling with increased valency of the cation and, with exceptions, with increased atomic weight.

I. Soaps that do not go into solution in xylene at 25°, give no evidence of swelling when the solvent is heated, but are quite soluble in the boiling solvent, and reprecipitate without evidence of jelly formation on cooling are: zinc stearate, copper palmitate, ferrous palmitate, and thallous palmitate. Lead palmitate probably belongs in this group.

II. Soaps that do not go into solution in xylene at 25° and show only slight swelling in the boiling solvent, remaining insoluble, are: sodium laurate, potassium palmitate, ferric oleate, and barium palmitate. Barium palmitate, in spite of its insolubility in boiling xylene, and its inability to form a jelly at any temperature, swells very appreciably in contact with hot xylene.

III. Soaps that do not go into solution in xylene at 25° but swell and go into solution on heating and set to fairly firm jellies when cooled are: thorium palmitate and silver palmitate. A 0.2-0.5 per cent jelly of silver palmitate remains unaltered for weeks. It remains clear and becomes more elastic as nine tenths of the solvent is squeezed out by mechanical pressure. Thin

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[1] J. W. McBain and W. L. McClatchie: Accepted by J. Am. Chem. Soc. for August 1932.

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sheets of dried jelly increased in length and breadth by one third when exposed to xylene.

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IV. Soaps that do not go into solution in xylene at 25°, swell and form elastic jellies when heated to about 100°, but undergo syneresis on cooling are listed as follows in approximate order of increasing swelling at room temperature: lithium palmitate, sodium palmitate, potassium oleate, sodium stearate, calcium palmitate, sodium oleate, sodium erucate, and chromium palmitate. Dried samples of these jellies swell somewhat in xylene at 25°. In 1925 one of us (J. W. M.) with Dr. H. Harris found that Kahlbaum's sodium stearate heated in a closed tube with benzene to 105°-110° forms a transparent jelly which is seen to be isotropic between crossed nicols. Just below 105° crystallization sets in, liberating liquid. With a rise of temperature the jelly reforms and is therefore the most stable state above 105°. The jelly is homogeneous and elastic. With lemonene the behavior is exactly similar but the transition slower. Sodium oleate behaves similarly with benzene and xylene, but neither soap exhibited any signs of gelation with acetone or chloroform. We found that von Weimarn[1] had already described in detail similar observations with sodium oleate in toluene, xylene, and benzene as well as in cumene and cymene.[2] Some of his jellies of sodium oleate were so elastic that a rod of jelly could be bent into a complete circle and again resume its original form on release. Camphoryl phenyl thiosemicarbazide (like the arsenates or dibenzyl cystine with water) is quite different from our soaps in that the crystalline state is the stable one in the presence of toluene, benzene, ether, chloroform, and alcohol. We found that a jelly could be produced from a slight supersaturation, whereas von Weimarn has postulated large supersaturation as a necessary condition for gelation.

Sodium palmitate powder is unaffected by cold xylene but swells and becomes transparent on heating, dispersing to a very viscous sol much as described by von Weimarn for sodium oleate. On continued heating it sets to a quite stiff, transparent, elastic jelly between the concentrations 1 and 8 per cent. On cooling the jelly undergoes strong syneresis and breaks up entirely into small pieces on shaking. A nearly transparent sheet dried at 100° became more transparent and increased 30 per cent in weight through 18 hours contact with xylene at 20°. Such a sheet swelled twenty fold in three hours when exposed to the vapor of boiling xylene and was still swelling rapidly. Sodium stearate was similar to sodium palmitate with less syneresis and greater swelling at room temperature (90 per cent in 24 hours).

A still completely transparent sheet of sodium oleate jelly dried at 100° was brittle and non-elastic but increased in weight on contact with xylene at room temperature by 50 per cent in 2 hours and 150 per cent in 36 hours, giving a transparent, somewhat flexible jelly. Sodium erucate was similar with greater swelling of preformed jelly although the original sodium erucate was not affected by cold xylene in 2 days; at 40° it nearly doubles its volume in a few hours.

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[1] P. P. von Weimarn: "Die Allgemeinheit des Kolloidzustandes," Bd. I, 2 Aufl., 352-363 (1925); J. Russ. Phys.-Chem. Soc., **46**, 610, 624, 625 (1914); **47**, 2163 (1915).

[2] P. P. von Weimarn: J. Russ. Phys.-Chem. Soc., **48**, 532 (1916).

Calcium palmitate in the form of dried jelly did not swell in contact with xylene at room temperature. Chromium palmitate, however, swelled by 160 per cent in 4 hours under the same conditions.

V. Soaps that swell on heating at lower temperature than those of group IV, giving fairly fluid solutions in boiling xylene and setting to jellies, which undergo syneresis if cooled to sufficiently low temperatures, are: aluminium stearate, aluminium palmitate, and aluminium oleate (the only soap that swells without limit at room temperature). Dried samples of the jellies swell at room temperature. Aluminium stearate does not swell below about 50°. A dried sheet of jelly swelled 20 per cent in one hour, 50 per cent in 2 hours, at room temperature. Aluminium oleate, as dried jelly, swelled 190 per cent in half an hour at room temperature, being completely converted to a sol in a few days.

Aluminium Palmitate in Xylene[1]

50° is a somewhat characteristic temperature because when a 4 per cent mixture of the impure monopalmitate prepared from aqueous solution is warmed, it is at this temperature that the entire mixture, which has progressively swelled, forms a fairly firm, elastic, extensible jelly. At the boiling point, even a 10 per cent jelly shows unusual ability to flow. Cooled to −15°, however, 1-10 per cent jellies are firm and elastic, do not flow, but show syneresis, the liquid being not fully reimbibed until the samples are warmed to nearly 50°. This parallels the well-known hysteresis of aqueous gelatin or agar but with a much greater range. The jellies are quite unusually elastic. A jelly dried at 100° is completely transparent and during a two hours' contact with xylene increases in weight by 40 per cent at 20°, 100 per cent at 25°, 120 per cent at 30°, 600 per cent at 40°, and 900 per cent at 60°.

Solvents for Pure Silver Palmitate

I. *Solvents in which the soap is insoluble at room temperature, and not* appreciably so on heating to about 100° are: diethyl ether and diacetone alcohol.

II. Solvents in which the soap is not appreciably soluble when at room temperature, but is moderately soluble on heating to 100° are: diethylene glycol, cellosolve, α-bromonaphthalin, butyl stearate, benzoyl chloride, xylene, chlorobenzene, and dichlorobenzene. With the last three solvents weak jellies are produced on cooling.

III. *A solvent in which the soap is very soluble at room temperature is* triethanolamine.

Solvents for Sodium Palmitate

I. Solvents in which the soap is not appreciably soluble at the boiling point of the solvent are: ethyl methyl ketone, benzyl acetate, and benzaldehyde.

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[1] E. Markowicz (Farben-Ztg., 34, 326, 414, 503 (1928)) reported that aluminium soaps and resinates swell in benzene derivatives and their homologues.

II. Solvents in which the soap is soluble at the boiling point, giving at least a 2 per cent solution, but is insoluble or only slightly so at room temperature are: butyl nitrite, butyric acid, and acetophenone.

III. Solvents in which the soap is soluble at the boiling point and which give jellies at room temperature without marked syneresis are: chloracetaldehyde, paraffin oil, and amyl valerate.

IV. Solvents in which the soap swells to a gelatinous mass on heating and undergoes syneresis on cooling to room temperature are: diamyl ether, o-dichlorobenzene, bromobenzene, benzene, toluene, and xylene.

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Solvents for Aluminium Palmitate

I. Solvents in which the soap is insoluble in both the boiling and cold solvent are: water, ethyl alcohol, amyl alcohol, glycerine, diethyl ether, and acetone.

II. Solvents in which the soap is soluble both at the boiling point and on cooling are: nitrobenzene, amyl valerate, diethyl aniline, diamyl ether, chloroform, o-dichlorobenzene, benzene, toluene, and xylene. The last four solvents behave in a manner comparable to that described for xylene.

Conclusions

These experiments indicate that for the silver and aluminium soaps the best solvents are in general the least polar compounds, a result in accord with Whitby's statement[1] that silver soaps swell in rubber solvents. The sodium soaps, although soluble in polar solvents, also dissolve and form jellies in the non-polar solvents. Although a number of solvents were found for silver palmitate, none gave elastic jellies at ordinary temperatures, which usually in previous work with various soaps indicated swelling ability for the combination used.

Sorption Isotherms of Vapors with Aluminium Palmitate

Isotherms at 40° were observed with an aluminium palmitate which after extraction with dried ether contained 6.5 per cent of aluminium and 87.7 per cent fatty acid. It was used in the form of a dried jelly made by dissolving in xylene at 90° and evaporating at 50°, ending with evacuation for 8 hours at 50°-90°. Before inserting into the experimental vessel, they were evacuated for 24 hours and the vessel sealed. A sorption pipette was used of a simpler design than that subsequently published by Jenkins and Bennett.[2] The necessary corrections are made for the amount of solvent vapor in the dead space. Four or five days were allowed before the attainment of equilibrium in each case. The results are given in Fig. 1.

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[1] G. S. Whitby: Colloid Symposium Monograph (Cambridge, 1926), 4, 213 (1926).

[2] W. J. Jenkins and H. B. Bennett: J. Phys. Chem., 34, 2318 (1930).

It is seen from Fig. 1 that the aluminium soap sorbed distinctly more toluene than benzene and much more chloroform than either. This resembles the order of swelling of rubber in these three solvents. All three curves have the form that one of us has designated[1] as characteristic for vapors of a moderate solvent with a swelling colloid such as the cellulose esters.

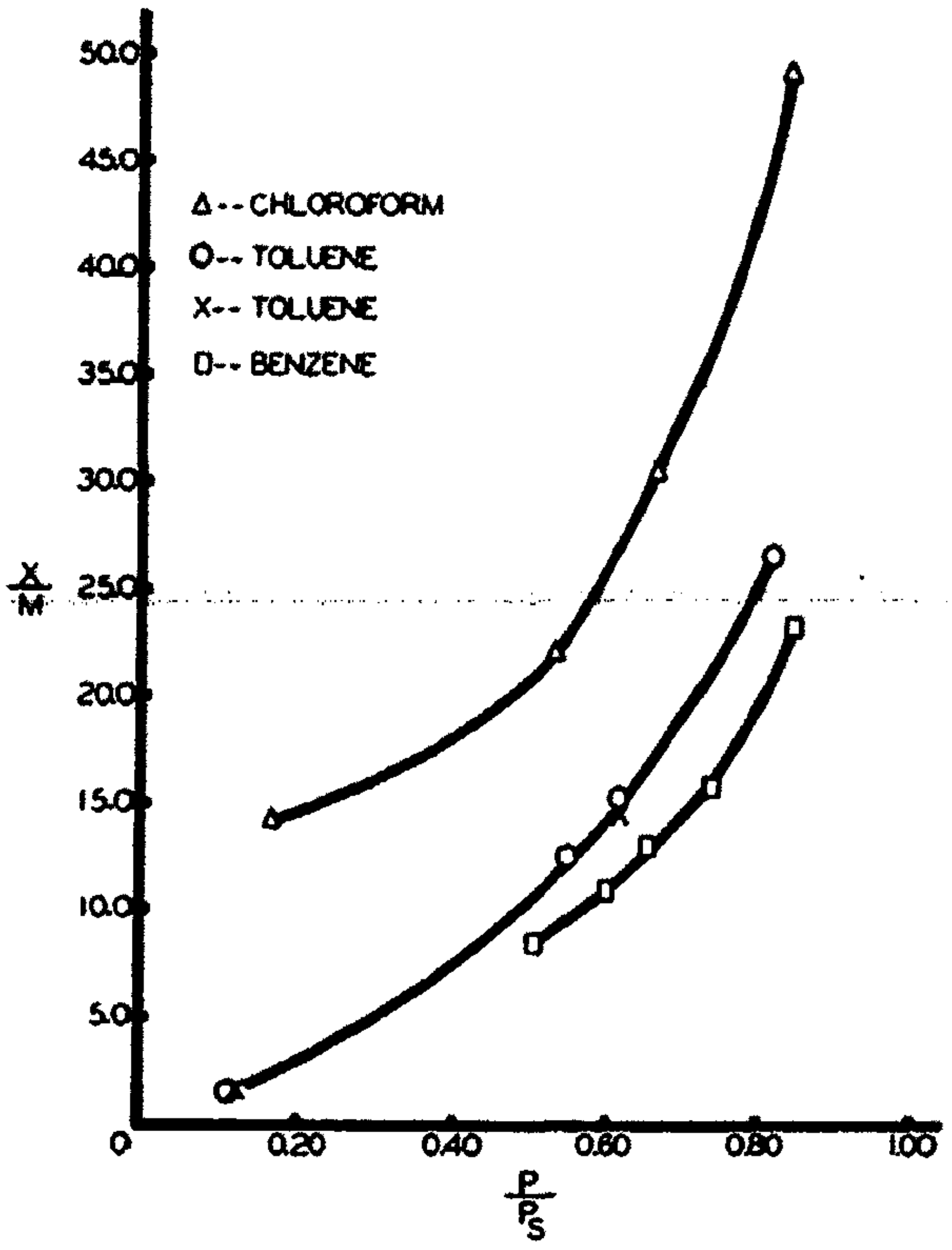

Fig. 1

The sorption of vapors by an aluminium palmitate intermediate between mono- and dipalmitate. Grams sorbed per 100 grams of soap, x/m, are plotted against relative humidities, p/p_s. The two crosses represent points on an independent isotherm with toluene.

Summary

The theory and mechanism of swelling and gelation is discussed. Numerous observations with metallic soaps and organic solvents illustrate theoretical points.

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California.

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[1] J. W. McBain: "Sorption of Gases and Vapours by Solids," 372 (1932).

THE SCATTERING OF LIGHT*

BY WILDER D. BANCROFT AND CHARLES GURCHOT

Over sixty years ago Lord Rayleigh[1] worked out a theory for the color of light scattered by fine particles. "It is now, I believe, generally admitted that the light which we receive from the clear sky is due in one way or another to small suspended particles which divert the light from its regular course. On this point the experiments of Tyndall with precipitated clouds seem quite decisive. Whenever the particles of the foreign matter are sufficiently fine, the light emitted laterally is blue in colour [now called Tyndall blue], and, in a direction perpendicular to that of the lateral beam, is *completely polarized*. . .

"Having disposed of the polarization, let us now consider how the intensity of the scattered light varies from one part of the spectrum to another, still supposing that all the particles are many times smaller than the wave-length even of violet light. The whole question admits of mathematical treatment; but, before entering upon that, it may be worth while to show how the principal result may be anticipated from a consideration of the *dimensions* of the quantities concerned.

"The object is to compare the intensities of the incident and scattered rays; for these will clearly be proportional. The number (i) expressing the ratio of the two amplitudes is a function of the following quantities:—T, the volume of the disturbing particles; r, the distance of the point under consideration from it; λ, the wave-length; b, the velocity of propagation of light; D and D', the original and altered densities; of which the first three depended only on space, the fourth on space and time, while the fifth and sixth introduce the conception of mass. Other elements of the problem there are none, except mere numbers and angles, which do not depend on the fundamental measurements of space, time, and mass. Since the ratio i, whose expression we seek, is of no dimensions in mass, it follows at once that D and D' only occur under the form $D:D'$, which is a simple number and may therefore be omitted. It remains to find how i varies with T, r, λ, b.

"Now of these quantities, b is the only one depending on time; and therefore, as i is of no dimensions in time, b cannot occur in its expression. We are left then with T, r, and λ; and from what we know of the dynamics of the question, we may be sure that i varies directly as T and inversely as r, and must therefore be proportional to $T \div \lambda^2 r$, T being of three dimensions in space. In passing from one part of the spectrum to another, λ is the only quantity which varies, and we have the important law:—

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*This work has been done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Phil. Mag., (4) 41, 107, 274 (1871).

When light is scattered by particles which are very small compared with any of the wave-lengths, the ratio of the amplitudes of the vibrations of the scattered and incident light varies inversely as the square of the wave-length and the intensity of the lights themselves as the inverse fourth power.

"I will now investigate the mathematical expression for the disturbance propagated in any direction from a small particle which a beam of light strikes.

"Let the vibration corresponding to the incident light be expressed by $A\cos(2\pi bt/\lambda)$. The acceleration is

$$-A\left(\frac{2\pi}{\lambda}b\right)^2\cos\frac{2\pi}{\lambda}bt;$$

so that the force which would have to be applied to the parts where the density is D', in order that the wave might pass on undisturbed, is per unit of volume,

$$-(D'-D)A\left(\frac{2\pi b}{\lambda}\right)^2\cos\frac{2\pi}{\lambda}bt.$$

To obtain the total force which must be supposed to act over the space occupied by the particle, the factor T must be introduced. The opposite of this conceived to act at O (the position of the particle) gives the same disturbance in the medium as is actually caused by the presence of the particle. Suppose, now, that the ray is incident along OY, and that the direction of vibration makes an angle α with the axis of x, which is the line of the scattered ray under consideration—a supposition which involves no loss of generality, because of the symmetry which we have shown to exist round the line of action of the force. The question is now entirely reduced to the discovery of the disturbance produced in the aether by a given periodic force acting at a fixed point in it. In his valuable paper 'On the Dynamical Theory of Diffraction,' Professor Stokes[1] has given a complete investigation of this problem; and I might assume the result at once. The method there used is, however, for this particular purpose very indirect, and accordingly I have thought it advisable to give a comparatively short cut to the result, which will be found at the end of the present paper. It is proved that if the total force acting at O in the manner supposed be $F\cos(2\pi bt/\lambda)$, the resulting disturbance in the ray propagated along OX is

$$\zeta=\frac{F\sin\alpha}{4\pi b^2Dr}\cos\frac{2\pi}{\lambda}(bt-r).$$

Substituting for F its value, we have

$$\zeta=A\frac{D'-D}{D}\cdot\frac{\pi T}{r\lambda^2}\sin\alpha\cos\frac{2\pi}{\lambda}(bt-r),$$

an equation which includes all our previous results and more."

"So much for a single particle. In actual experiments, as for instance with Professor Tyndall's 'clouds', we have to deal with an immense number of such particles; and the question now is to deduce what their effect must be

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[1] Cambridge Phil. Trans., 9, 1 (1849).

from the results already obtained. Were the particles absolutely motionless, the partial waves sent out in any direction from them would have permanent relations as to phase, and the total disturbance would have to be found by compounding the *vibrations* due to all the particles. Such a supposition, however, would be very wide of the mark; for, in consequence of the extreme smallness of λ, the slightest motion of any particle will cause an alteration of phase passing through many periods in less time than the eye could appreciate. Our particles are, then, to be treated as so many *unconnected* sources of light; and instead of adding the *vibrations*, we must take the *intensities* represented by their squares. Only in one direction is a different treatment necessary, namely along the course of the primary light. I mention this because it would not otherwise appear how the reduction in the intensity of the transmitted light is effected; but we do not require to follow the details of the process, because when once we know the intensity of the light emitted laterally, the principle of energy will tell us what the primary wave has lost.

"The intensity of the light scattered from a cloud is thus equal to

$$A^2 \frac{(D' - D)^2}{D^2} \sin^2 \alpha \frac{\pi^2 \Sigma T^2}{\lambda^4 r^2}.$$

where ΣT^2 is the sum of all the squares of T. If T^2 be understood to denote the mean square of T (*not* the square of the mean value of T), and m the number of particles, $\Sigma T^2 = m\,T$.[2] If the primary light be unpolarized, the intensity in a direction making an angle β with its course becomes

$$A = \frac{(D' - D)^2}{D^2} (1 + \cos^2\beta) \frac{m\pi T^2}{\lambda^4 D^2}.$$

"The principle of energy makes it clear that the light emitted laterally is not a new creation, but only diverted from the main stream. If T represents the intensity of the primary light after traversing a thickness x of the turbid medium, we have $dT = -kT\lambda^{-4} \frac{dx,}{-k\lambda^{-4}x}$ where k is a constant independent of λ. On integration, $I = I_0\epsilon$, if I_0 correspond to $x = 0$,—a law altogether similar to that of absorption, and showing how the light tends to become yellow and finally red as the thickness of the medium increases."

These equations show that the light scattered at right angles is always richer in the shorter wave-lengths, while the transmitted light is always richer in the longer wave-lengths. For very fine particles the scattered light will be a violet-blue changing to blue as the particles get larger. When the particles are no longer small relatively to the wave-length, ordinary reflection will come in and there may be enough white light to mask the blue. The Rayleigh theory has stood the test of experiment for over sixty years, which is doing well and which is extraordinary in view of the fact that data were published forty years ago which were sufficient, had people paid attention to them, to have proved that the Rayleigh theory cannot be adequate.

In 1892 Aitken[1] published his study of the transmitted colors in the case of condensation, using both a steam jet and an expansion apparatus. "As has

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[1] Proc. Roy. Soc., 51, 408 (1892).

been stated, a slight expansion produces a blue colour if the number of particles be small, and if the expansion be increased after the blue is produced, the colour changes; and we shall now describe the successive colours, which appear as the degree of expansion is increased, that is, as the size of the water particles is increased. When the expansion begins, blue is the first distinct colour to appear; but very pale yellow and slightly reddish colours have been noticed before the expansion was sufficient to produce the blue. These reddish colours can be seen very distinctly when we use an excessively great number of particles, and they are best seen with gas light. These reddish colours change imperceptibly into blue as the expansion is increased, and the blue in turn changes by minute degrees into green with further expansion, and the green in turn changes to yellow; then a brownish colour appears which changes to a somewhat mixed purple; then the blue returns again, to be followed by green and yellow as the expansion is still further increased. It is not easy to get this sequence of colours carried so far. Sometimes one stroke of the pump only carries the colour on to yellow; sometimes it may go to the second blue or green, but less frequently to the second yellow. The final colour depends on the number of particles present. It is necessary to have a good many drops, so that the colour may be distinct, and yet not too many, or the expansion may not be sufficient to grow the particles large enough to give the second series of colours. It is found that a high expansion, produced by two or more strokes of the pump, does not give satisfactory results.

"To observe the effect of temperature on these colour phenomena, another tube was prepared with glass ends and jacketed, so that the air in it might be heated or cooled to any desired temperature. The result was very much what might have been expected: at the different temperatures all the colours made their appearance in the usual order; but there was a considerable difference in the amount of expansion required to produce a given colour with change of temperature. At a high temperature each of the colours appeared with a less expansion than the temperature was low. [This means that at the higher temperature a given expansion produces larger drops.] In making these tests the number of dust particles in the air must be kept as constant as possible. For this purpose windows and doors should be kept closed for some time before beginning, and the experiments should be repeated without change of conditions. When the air was cooled to about 35°, it took two strokes of the pump to develop a full blue, and three strokes made it only green. At a temperature a little over 50°, two strokes made it green, while if the air was heated to about 80°, two strokes sent it past blue and green and on to yellow, and less than one stroke made it full blue. These differences are due to more vapour being present and being condensed, with the same amount of expansion, when the air is hot than when it is cold. It should be stated that in all cases the air was saturated, the inside of the tube being wet."

"These experiments show that the colour produced by the small drops of water depends on the size of the drops, and the depth of the colour on their number. But it is not so easy to follow the manner in which the drops produce the colour. If we take the simplest case, we can easily see how part, at least, of the colour is produced. In the steam jet condensing dense, and colouring the transmitted light yellow, part of the effect is no doubt due to some of the particles in that form of condensation being so small that they reflect and scatter the shorter waves of light, while they allow the longer ones to pass through. The colour in this case is partly caused in the same way as the yellow produced by small particles suspended in liquids, as in Brücke's experiments with mastic, or as when silver chloride is formed from a solution of the nitrate. The light reflected by the liquids in these experiments is of a bluish tint, complementary to the yellow light transmitted by them, and this blue light is polarised. It has been found that, when the steam jet is of a good yellow by transmitted light it reflects a good deal of a bluish light; and further, this blue light is polarised in the same way as the light from the small particles in the experiments with liquids.

"While this explanation helps us to understand the manner in which the yellow light is produced in the steam jets, yet it fails to explain the succession of colours seen in the expansion experiments, where blue first appears, then green and yellow; and when the expansion is still further increased, the blue again returns to give place to a second green and yellow. The most probable explanation of these colour phenomena is that they are produced in the same way as the colours in plates, somewhat after the manner Newton thought the colour of the sky was produced. The order of succession of the colours in thin plates is the same as in these condensation phenomena. As no white follows the first blue, it seems probable that the first spectrum, or order of colours, is not observed; that the two generally seen are the second and third."

With increasing size of drops the transmitted colors apparently vary: yellow, red, blue, green, yellow, brown, purple, blue, green, yellow. This would be quite regular if the brown had been a red. Regardless of that, there are certainly two blues and apparently three yellows, a result that cannot possibly be deduced from Rayleigh's equations. Five years earlier R. von Helmholtz[1] reported that the light scattered by a steam jet varied with increasing size of drops: blue, whitish, purple, red, yellow, green, pale blue. These studies were carried much farther by Barus[2] whose data are given in Table I.

At the time, Barus said that "there can be no doubt that the succession of the colors of cloudy condensation is identical with the corresponding succession in Newton's rings of the first and second order, seen by transmitted light under normal incidence."

In 1902 Barus[3] said: "It may be noted that the order of size of particle is about ten times longer than would follow if the same (axial) colour were produced by interference in thin plates. . . . The axial colours vanish completely (become white) before even one half of the coronas have been passed. Experiment shows, therefore, conformably with the given interpretation that the condition of optical saturation (removal of the original white light) is a line of vision quite blocked by water particles all of rigorously the same size.

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[1] Wied. Ann., 32, 1 (1887).

[2] Am. Meteorol. J., 9, 488 (1893).

[3] Phil. Mag., (6) 4, 24 (1902).

Table I

Transmitted Colors of Drops of Water

Color of jets	Interference colors	Thickness of air plate, μ
White	White	0.02
Yellow	Yellow white	0.048
	Brown white	0.079
Orange	Yellow brown	0.109
Brown	Brown	0.117
Opaque	Red	0.129
Opaque	Carmine	0.133
Opaque	Dark-red brown	0.137
Dark violet	Dark violet	0.140
Indigo	Indigo	0.153
Blue	Blue	0.166
Gray blue	Gray blue	0.215
Blue green	Blue green	0.252
Green	Pale green	0.268
	Yellow green	0.275
Green yellow	Yellow green	0.282
	Green yellow	0.287
Straw yellow	Yellow	0.294
	Orange	0.332
Muddy brown	Brown orange	0.364
	Light carmine	0.374
Pale purple	Purple	0.413
Pale violet purple	Violet purple	0.421
Pale violet	Violet	0.433
Pale indigo	Indigo	0.455
	Dark blue	0.474
Faint green	Green blue	0.499
	Green	0.550
Faint yellow green	Yellow green	0.554
	Dull yellow	0.575

Thus it would seem as if each single water particle colours the area of its projection.

"Now what kind of absorption is this which occurs for particles of such surprisingly large dimensions relatively to the wave-length of light, which occurs moreover in just as marked a degree if the particles are electrical insulators like the precipitates from benzine and petroleum vapours? For though one cannot regard a water particle captured by a saline nucleus as quite an insulator, there seems to be no electrical conduction possible for the case where a sulphur nucleus condenses benzine vapour." In a later paper Barus[1] revises his figures a little and gets value of 6-9 for the ratio d/D, where d is the diameter of the fog particles and D the thickness of an air plate

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[1] Am. J. Sci., (4) 25, 224 (1908).

giving like interference colors. "From this it appears that the strong axial blues of the first order must belong to particles even larger than 0.0001 cm [$> 1\mu$] in diameter, and that all particles are more than six times larger than would be demanded for interference.

"Recently I have considered the case of a lamellar grating, in which diffractions are obtained from a uniform succession of alternately different thicknesses of clear glass. Experiments with such gratings were originally made by Quincke and there is a full theoretical treatment by Verdet. The behavior of this grating differs from that of the usual kind in the occurrence of an additional factor

$$\cos^2 (\pi d(n - 1) + \pi a \sin \delta)/A$$

where n is the index of refraction, d the difference in thickness between thin strips of width a and of thick strips of width b, δ the angle of diffraction. Hence for axial color, $\delta = 0$, minima occur at $(n - 1)d = (2m + 1)\lambda/2$, whereas for Newton interferences the minima occur for a thickness of D in case of transmitted light, where $2\mu D = (2m + 1)\lambda/2$; whence $d/D = 2n/(n-1)$. In case of water $n = 1.33$ or $d/D = 8.0$. This result, holding for a grating of transparent strips, is so near the above datum $d/D 76$ for a medium of transparent particles (for which there is no theory), that it seems reasonable to conclude that the actual colors are referable to the same type of phenomenon in both cases. The need of observations through long columns in case of fog particles suspended in air is additionally confirmative, since the contribution of color due to one particle must be exceedingly small."

Similar phenomena have been observed in every-day life. Piazzi Smyth[1] reports that for several days in India the disk of the sun appeared blue or green in the morning and evening. Aitken[2] considers this as due to the presence of drops of water of the right size. He reports that Principal Forbes observed colors in the steam escaping from a safety valve and Mr. Lockyer,[3] when on Windermere, saw the sun of a vivid green through the steam of a little paddle-wheel steamer. Whymper[4] saw a green sun through volcanic dust from Cotopaxi. Blanc[5] showed that a ripened photographic emulsion transmits a blue image of the sun. Keen and Porter[6] have shown that very fine particles of colloidal sulphur scatter blue and transmit red preponderantly, just as they should; but they transmit blue at some stage in the agglomeration. The explanation offered by Raman and Ray[7] accounts for the decreased opacity but not for the blue color. Wolfgang Ostwald and Auerbach[8] have found a color series for sulphur of blue, green, yellow, orange, red, violet, blue, which is perfectly satisfactory except that they consider the first two colors as due to sulphur in true solution. This is probably an error.

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[1] Trans. Roy. Soc. Edinburgh, **32**, 389 (1884).

[2] "Collected Scientific Papers," 270 (1923).

[3] Nature, **28**, 155 (1883).

[4] Travels among the Great Andes of the Equator," 324 (1892).

[5] Bull. Soc. franç. Photographie, (2) **17**, 256 (1911).

[6] Proc. Roy. Soc., **89A**, 370; Rayleigh: **90A**, 219 (1916); Auerbach: Kolloid-Z., **27**, 223 (1920).

[7] Proc. Roy. Soc., **100A**, 102 (1921).

[8] Kolloidchem. Beihefte, **30**, 336 (1926).

Harrison[1] explains the colors of the starch-iodide complex as a phenomenon of dispersion, meaning scattering. "An alcoholic suspension of starch is mixed with an alcoholic solution of iodine until there is a distinct yellow color. On adding water the color changes to orange, red, and violet, becoming blue on extreme dilution. On adding alcohol to a blue solution of starch and iodine the color changes reverse, winding up with a yellow." This is a very important experimental observation; but it is not clear whether it is the starch or the iodine that is being dispersed.

We have checked up on some of the points involved. When an equal volume of 0.106 M HCl is added to a 0.051 M sodium thiosulphate solution, the mixture goes through the following color changes when viewed by transmitted light. Almost immediately it becomes a pale yellow, turning to orange, which changes to red in about thirty minutes and then becomes purplish. By this time the solution has become decidedly opaque. At the end of an hour the solution is too opaque to transmit light appreciably from an incandescent lamp or even from the sun. After about eighty minutes the solution begins to clear to a beautiful blue solution showing almost no sign of turbidity. This blue persists from one hour to six hours, the time varying with the preparation. Sometimes the solution shows no more color changes, the sulphur settling out gradually and leaving the supernatant liquid clear and colorless. If one is lucky however, the color changes from blue to greenish-blue, green, or lavender. In all cases the sulphur has settled and the solution has become colorless at the end of sixteen to twenty-four hours. More dilute solutions show about the same changes of color; but the color is less intense.

The best effect is produced when the source of light is distant and fairly well circumscribed, such as the sun or a distant window. Although electric light filaments do very well (they alone being colored), a point source is neither necessary nor desirable if a larger source is available. When the solution is diluted with water at any color stage, the color changes in intensity only, becoming paler. This indicates that the distance between the particles is not a factor in producing the color. Our results confirm those of Aitken and of Barus.

Special titration experiments showed that the sulphur is precipitated practically completely at the start and that the increase in size of the particles must therefore be accompanied by a corresponding decrease in the number. The reflected colors in these preparations are always complementary to the transmitted colors, as is shown in Table II in which is recorded a run that went faster than usual.

When examined under the microscope the sulphur particles are seen as perfect spheres. The particles in the solutions transmitting yellow are about 0.2μ in diameter. They are about 0.5μ in the red solutions, 1-2μ in the blue solutions, and 3-4μ in the green solutions.

There is some evidence that the color varies with the refractive index of the medium, smaller particles giving a blue when the index of refraction is less. A corollary of this is that, in a medium with a higher refractive index than

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[1] Kolloid-Z., 9, 5 (1911).

TABLE II

Colors of Sulphur Sols

Min.	Transmitted	Reflected
1	Yellow	Blue
2	Orange	Blue
3	Deep orange	Blue
4	Red	Greenish blue
7	Deep red (opaque)	Greenish blue
9	Purple	?
10-15	Bluish purple	Yellowish red
20	Deep blue	Orange red
25	Greenish blue	Orange red
30	Green	Red
35	Light green	Pink

water, the transmitted light should be displaced toward the red. This was found to be the case. The thiosulphate solution was prepared in one percent agar and a layer 1 mm thick was allowed to set to a jelly. This layer was immersed in a hydrochloric acid solution and it then passed through the usual color changes, though relatively slowly. When the blue stage was reached the film was removed, washed and allowed to dry. It was then a dirty red by transmitted light. Addition of a drop of water to any part of the film produced a deep blue spot, the red color reappearing on drying. This could be repeated at will. The dried film was then shaved down with a razor blade until the microscope showed only a single layer of sulphur particles present. The color was still red, though not so intense.

Films of a one percent agar jelly containing sodium thiosulphate were made about 0.5 mm thick and were covered with rectangular pieces of glass. They were allowed to stand for twenty-four hours in a hydrochloric acid solution. A gradation of colors was obtained with red at the edges and blue towards the center of the film. In addition there could be seen a well-defined repetition of the colors, so that within the width of 1 cm in some slides as many as three complete color series could be seen, each ranging from yellow to green. A clear space was left in the middle of the film about 0.5 cm wide. When these jelly preparations were kept moist, they retained their colors for about a month.

The following variation produced sulphur films showing reds and blues which are permanent. A layer of jelly ten centimeters square and about 1 mm thick on a glass plate was covered with another glass plate supported at the corners by thin pieces of cork and immersed in hydrochloric acid solution for twenty-four hours in the usual way. The cover plate was removed carefully. When the film was washed and allowed to dry, portions of it showed a beautiful transmitted blue. The colors in this case are best seen by means of a frosted electric light bulb. The blues must originate with some color in the higher series. When the refractive index of agar is increased by drying a lower order blue is observed.

A similar agar jelly in test tubes, overlaid with a hydrochloric acid solution, gives beautifully colored rings, simulating Liesegang rings and changing from reds to blues and greens as one looks through different portions of the tube. These jelly cylinders can be slipped out of the tubes and slices cut out at the differently colored layers. A cube of green jelly was cut out and allowed to soak in glycerine until all the water was displaced. The jelly turned blue. On replacing it in water so that the glycerine was displaced, the jelly turned green again.

When slices of blue and green jelly were allowed to dry, they turned various shades of orange and red. Wetting the layers restored the original colors. When examined under the microscope the sulphur particles appeared as perfect spheres with light centers. They were closely surrounded by a thin colored ring which was the same color as that of the entire mass. This makes it clear why the distance between the particles affects only the depth of color and not the hue.

Dry films of sulphur which show good transmitted blues can be obtained by subliming the sulphur on glass. Barium sulphate can be precipitated on glass so as to transmit blue. When these were painted with collodion, they turned red when still wet. An emulsion of lanolin in water showed a transmitted red when squeezed between glass plates. If the film is heated carefully the transmitted light changes to blue. When more pressure was put on the plates the red color returned.

TABLE III

Transmitted Colors of Different Sols

Substance	Color	Particle Size	Refracture Index
Sulphur	Red	0.5μ	1.93
	Blue	1-2μ	
	Green	3-4μ	
Zinc oxide	Red	0.1-0.15μ	2.03
	Purple	0.5-1μ	
Silver bromide	Red	0.1μ	2.25
	Green	0.5μ	
Copper oxide	Red	0.1-0.5μ	2.70
	Blue	1-2μ	
Carbon black	Red	0.1-0.5μ	2.42
	Blue	1μ	
Selenium	Blue	0.5μ	2.9
Silver	Yellow	0.09μ	0.16
	Violet	0.15μ	
	Blue-green	0.18μ	
Gold	Red	0.01-0.04μ	0.37
	Blue	0.08μ	
Copper	Red	<0.1μ	0.64

Experiments were made with various suspensions in water to determine approximately the relation between color and particle size. The color data given in Table III refer to transmitted light.

The values for transmitted blue are not very different for sulphur, zinc oxide, copper oxide, and carbon black. They agree well with the values found by Barus for water, which indicates that the refractive index of the particles has relatively little effect on the color. The values for silver bromide and for selenium are lower. No explanation of this will be attempted at present. With silver, copper and gold the blue occurs at a very much smaller diameter than in the case of the other substances. Two characteristics of these three metals are great opacity and abnormally low apparent indices of refraction. For the time being, we are laying more stress on the opacity than on the apparent indices of refraction.

There is still no theory of the phenomena and apparently no question as to the phenomena. We have tried for six years to get physicists interested in the problem, but in vain. It is not a fashionable problem at the present time. We, of course, do not know enough about the mathematical theory of light to solve the problem ourselves and it therefore seems wise to formulate the problem now as we see it in the hope that some day some physicist will clean up the whole thing.

Since Rayleigh's theory describes the facts pretty well over a certain range and since it does not account for the periodicity which has been shown to occur, it is pretty clear that the real formulation, when it comes, must take account of the recurrent nature of the phenomena and must reduce to something equivalent to the Rayleigh formula over a certain range of diameters. Pending the discovery of such an equation, let us consider only three colors for the moment and let us make the empirical assumption that with increasing size of particle the colors by transmitted light change yellow, red, blue, yellow, red, blue, yellow, red, blue, indefinitely until some other factor becomes predominant. All color due to scattering disappears when the suspended particles become small enough. When the particles become sufficiently large, we get the ordinary phenomena of reflection and refraction. We will make the additional, plausible assumption that the disappearance of all color due to suspended particles occurs at smaller diameters the more opaque the particle is.

On this basis the colors of colloidal gold and colloidal silver are similar in nature to the colors of the steam jets studied by R. von Helmholtz, Aitken, and Barus among others. The difference is merely that we are dealing with a different cycle in the cases of the metals. If this is true, particles of silver of the general order of 1-2μ in diameter should transmit blue light. These would not stay up in water; but the experiment could be tried in an agar or gelatine jelly. A necessary consequence of the general hypothesis is that it should be possible to prepare yellow, red, and blue sols of any metal whatsoever, provided it is stable in the medium. This seems to be true in general, though there are some gaps in our knowledge and there may be other factors coming in.

Yellow, red and blue sols of silver, mercury, gold, copper and selenium have been reported, though the yellow sols of gold and copper and the blue sols of selenium are not easy to make. Yellow and red sols of platinum are known. Probably a complete set could be prepared if necessary. Sodium fogs transmit yellow, a color which the vapor absorbs. Sodium and potassium salts may be colored blue by cathode rays.

Wolfgang Ostwald[1] points out that "with all the colloids studied—and therefore probably according to some law—the maximum absorption is displaced with increasing dispersity of the colloid towards the region of shorter wave-lengths." He illustrates this by the case of gold, for which the transmitted light varies with decreasing dispersity of the gold in the order: yellow, orange, red, violet, blue, green. Ostwald has ignored the cyclic nature of the phenomenon although he is familiar with the work of Barus. Ostwald[2] puts gold sols and drops of water in two different categories, which seems unwise.

The experiments of Kirchner and Zsigmondy[3] on colloidal gold in gelatine agree with those of Faraday[4] but do not agree with our experiments on sulphur in agar. Some of the gold sols changed from red to blue on drying and went back to red when moistened. The sulphur jellies went from blue to red on drying and back to blue when moistened. A special investigation will be necessary in order to account for the apparent discrepancy. Kirchner explained the color change on the basis of Planck's dispersion theory for isotropic dielectrics. He regarded the particles as resonators, which behaved differently when in close proximity. This cannot be true because all experiments show that the distance between the particles affects only the intensity of the color.

Mulliken[5] reports that cholesterin benzoate crystallizes in pearly white leaflets which fuse to a turbid liquid at 145.5° (uncorrected). At 178.5° (uncorrected) the turbidity suddenly disappears. In cooling, a brilliant display of opalescent colors is exhibited, among which a brilliant blue, appearing at about the temperature of the higher melting point, followed by a violet-blue just before complete solidification, are the most prominent. The colors disappear very quickly." It was hoped that these colors might be due to scattered light of the type that we have been considering; but this is not the case.

When cholesterin benzoate is fused and allowed to cool, it goes through a series of beautiful iridescent colors which disappear when the compound has finally solidified. The iridescence is due to the formation of liquid crystals which form on cooling and which give brilliant polarization colors under the microscope. We are apparently dealing with the Christiansen affect. Cholesterin acetate gives less marked color changes than the benzoate; but a 1:1 mixture of the two gives iridescent colors on cooling from the melt which are much more brilliant than those from the benzoate alone. A eutectic mixture is formed which melts at a much lower temperature than either of the components.

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[1] Kolloidchem. Beihefte, **2**, 409 (1911).

[2] "Licht und Farbe in Kolloiden," 347, 427 (1924).

[3] Ann. Physik, (4) **15**, 573 (1904).

[4] Phil. Trans., **147**, 175 (1857).

[5] "A Method for the Identification of Pure Organic Compounds," **1**, 172 (1904).

The general results of this paper are as follows:—

1. With drops of water the colors by transmitted light change periodically with varying size of the drops.

2. A transmitted blue is obtained when the diameters are 1-2μ.

3. A similar blue is obtained with many solids at approximately the same diameters.

4. The colors of such particles do not seem to vary appreciably with the indices of refraction of the particles but do vary considerably with changing index of refraction of the surrounding medium.

5. The color changes with changing particle sizes show an astonishing parallelism with interference colors.

6. It is not known whether an adsorbed film takes part in the production of the colors.

7. The colors of the colloidal metals do not depend primarily on the nature of the metal. It is probable that one can make yellow, red, and blue sols of any metal.

8. The colors of colloidal metals seem to be identical in nature with the colors of particles of water or sulphur, but can occur at much smaller diameters.

9. It is probable that the colors of colloidal metals represent another cycle in the water series, made possible by the extreme opacity of the metallic particles.

10. Since the Rayleigh equations for the scattering of light by particles small relatively to the wave-lengths of light do not account for the periodic changes which actually occur, the Rayleigh equations cannot be an accurate statement of things as they are.

11. Since the Rayleigh equations do describe the facts very well over a limited range of diameters, it is probable that the true equations will become practically equivalent to the Rayleigh equations for the same range of particle sizes.

12. The effect of drying gold sols in gelatine is apparently different from the effect of drying sulphur sols suspended in agar. Special experiments are called for to determine whether the discrepancy is due to the difference between gold and sulphur, is due to the difference between gelatine and agar, or is due to experimental error.

Cornell University.

NITROGEN COMPOUNDS OF GALLIUM

I. The Ammonates of Gallium Tribromide and Gallium Triiodide

II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia*

BY WARREN C. JOHNSON AND JAMES B. PARSONS

The halides of the elements of the third group, namely, boron, aluminium, gallium, indium and thallium, appear to show divergent properties in their behavior toward ammonia. In general, the halide reacts with ammonia gas or liquid ammonia to form an addition compound (ammonate). As an alternative, the halide may be partially or completely ammonolyzed with the formation of the ammonium salt of the halogen and the amide or imide of the metal. Whether or not the ammonolytic reaction will proceed is dependent in a large measure upon the nature of the cation in combination with the halogen.

Boron trifluoride[1] combines with one molecule of ammonia to form an ammonate which has recently been shown to be appreciably ammonolyzed[2] in liquid ammonia solution. The trichloride,[3] tribromide[4] and triiodide[5] of boron form ammonates with ammonia at low temperatures but readily undergo ammonolysis at slightly elevated temperatures. All the halides of aluminum [6,7,8] form ammonates with no indication of ammonolysis. The corresponding salts of indium[9] and thallium,[10] with the exception of the fluorides, behave similarly.

Gallium occupies an intermediate position in the third group of elements. Since it is more electropositive in nature than aluminium, one would predict its salts to be stable in liquid ammonia, particularly at low temperatures. The following work was undertaken to determine some of the properties of the halides of gallium in liquid ammonia solution.

Experimental

The halides of gallium were prepared by the direct combination of the elements according to a previously described method.[11] The tribromide and triiodide of gallium were selected since appreciable quantities of these salts were available. Liquid ammonia, dried over sodium in small steel cylinders, was employed in all experiments.

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* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

[1] Mixter: Am. Chem. J., 2, 153 (1880).

[2] Kraus and Brown: J. Am. Chem. Soc., 51, 2690 (1929).

[3] Joannis: Compt. rend., 135, 1106 (1902).

[4] Besson: Compt. rend., 112, 1002; 113, 78 (1891); Stock: Ber., 34, 949 (1901).

[5] Besson: loc. cit.; Joannis: loc. cit.

[6] Clark: Am. J. Sci., (5) 7, 1 (1924).

[7] Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," 5, 319-20, 326 (1924).

[8] Franklin: J. Am. Chem. Soc., 27, 847 (1905).

[9] Klemm: Z. anorg. Chem., 163, 240 (1927).

[10] Biltz and Stollenwerk: Z. anorg. Chem., 119, 97 (1921).

[11] Johnson and Parsons: J. Phys. Chem., 34, 1210 (1930).

Gallium Tribromide Hexammonate.

Dry ammonia gas was condensed at −33.5° on gallium tribromide in a tube which could be readily detached from a "vacuum line" and weighed. The usual technique was employed to prevent contact of the salt with air and moisture. Reaction followed immediately after the introduction of ammonia to produce a white powder which appeared to be only slightly soluble in liquid ammonia. After the mixture had been allowed to stand in contact with the ammonia for several hours, the excess ammonia was allowed to escape and the system was thoroughly evacuated. The tube and contents finally assumed a constant weight at room temperature. The following results were obtained for two different preparations.

TABLE I

The Formation of Gallium Tribromide Hexammonate

Weight of $GaBr_3$ grams	Weight of ammonia reacted (grams)	Ratio $NH_3/GaBr_3$ found
0.4865	0.1632	6.09
0.4690	0.1533	5.94

Although ammonia was removed from the compound in vacuo until the weight of the tube and contents assumed a constant value and the pressure was reduced to 10^{-4} mm., its odor could be detected when the ammonate was exposed to air. A sample of the material after exposure to air, was analyzed for ammonia by distillation from an alkaline solution into standard acid solution, and for bromine by the usual procedure. The ammonia content was found to correspond to approximately two-thirds of the total amount that had reacted with the gallium tribromide, while the bromine analysis agreed well with the calculated value.

Anal. Subst., 0.0553; NH_3, 0.0099; AgBr, 0.0756. Calcd. for $GaBr_3.6NH_3$, NH_3, 24.82; Br, 58.24. Found: 17.94, 58.17.

These facts indicate that while ammonia is lost on exposure of the ammonate to air, water replaces the ammonia so that the net change in weight is very small. However, this process was found to be readily reversible. When the material was again subjected to liquid ammonia and the excess ammonia removed as described above, analysis showed six molecules of ammonia to be in combination with the gallium tribromide.

In order to obtain pure samples of the ammonate for analysis, they were sealed off in small tubes attached to the reaction tube without exposure to the air. The tubes were then cracked with a piece of hot glass and finally broken in a Kjeldahl flask under the alkali solution. The results recorded below were obtained on two samples of the ammonate; sample I was exposed to air and then treated with liquid ammonia to restore the ammonate to its original condition, while sample II was prepared and manipulated in the absence of air and moisture.

Anal. Subst., I, 0.1062, II, 0.6221; NH_3, 0.0263, 0.1531. Calcd. for $GaBr_3.6NH_3$, NH_3, 24.82. Found: 24.74, 24.62.

Sample I was analyzed for bromine by the usual method.

Anal. Subst., 0.1062; AgBr, 0.1453. Calcd. for $GaBr_3.6NH_3$; Br, 58.24; Found: 58.22.

While the above values show the quantity of ammonia absorbed in the reaction, they do not indicate the nature or mechanism of the process. There are two possibilities:

(1) $GaBr_3 + 6\ NH_3 = GaBr_3.6NH_3$ (addition or ammonation).

(2) $GaBr_3 + 6\ NH_3 = Ga(NH_2)_3 + 3\ NH_4Br$ (ammonolysis).

If ammonolysis were to take place, the ammonium bromide, which is highly soluble in liquid ammonia, could be readily separated from the slightly soluble product of the reaction (presumably the amide or imide of gallium). Attempts to carry out such a separation were made as follows: a Pyrex tube about 1.5 cm. in diameter and 15 cm. in length was fitted with a side arm stopcock and a second leg of the same dimensions. A small amount of gallium tribromide was placed in the tube which was then sealed off and evacuated. Ammonia was condensed on the salt and the system was allowed to stand for several hours. The clear solution above the salt was carefully decanted into the second leg of the tube. A Dewar flask of ammonia was placed about the main portion of the tube and the ammonia distilled out of the leg to the original sample with the deposition of any material that may have dissolved. Ten such extractions were made until a quantity of the soluble portion sufficient for an analysis was obtained. An examination of this material proved it to be identical with gallium tribromide hexammonate. This experiment shows that ammonolysis does not take place and that the solvated salt is slightly soluble in liquid ammonia.

Additional proof for this result is based upon the fact that ammonium bromide is an acid in liquid ammonia and, when treated with a strongly electropositive metal such as sodium, liberates hydrogen according to the following equation:

$$NH_4Br + Na = NaBr + NH_3 + 1/2\ H_2.$$

Experiments showed, however, no indication of hydrogen gas when metallic sodium was added to a solution of gallium bromide in liquid ammonia. On the other hand, reduction of the salt to metallic gallium appeared to take place. According to the results of these experiments it is concluded that an ammonate, $GaBr_3.6NH_3$, is formed when gallium tribromide is subjected to liquid ammonia.

Properties. The ammonate is obtained as a white powder from liquid ammonia solution. In the absence of moisture it is remarkably stable. In moist air, water molecules replace the ammonia which is readily liberated as a gas. This process is found to be reversible; in other words, ammonia will replace the water in liquid ammonia solution. Dry air does not appear to have any effect upon the ammonate. It is easily soluble in alkali and hydrochloric acid solutions. At higher temperatures, about 100°C, the ammonate slowly loses ammonia when subjected to a high vacuum. The ammonate exhibits an appreciable solubility in liquid ammonia.

Gallium Triiodide Hexammonate.

Gallium triiodide was treated with liquid ammonia in a manner analogous to that employed in the bromide investigation described above. A reaction was found to proceed rapidly with the formation of gallium triiodide hexammonate as is indicated by the following results:

Table II

The Formation of Gallium Triiodide Hexammonate

Weight of GaI_3, g.	Weight of ammonia reacted, g.	Ratio NH_3/GaI_3 found
0.8728	0.1981	6.00
0.5087	0.1142	5.94

When the ammonate was exposed to air, ammonia was liberated but was found to be restored as in the case of the bromide by a second treatment with liquid ammonia. The product exposed to air was analyzed for ammonia:

Anal. Subst., 0.3351. NH_3, 0.0549. Calcd. for $GaI_3.6NH_3$; NH_3, 18.49. Found: 16.39.

Another portion of the product exposed to air was restored to its original condition in liquid ammonia, the ammonate was freed of the excess ammonia and finally analyzed.

Anal. Subst., 0.2430; NH_3, 0.0453. Calcd. for $GaI_3.6NH_3$; NH_3, 18.49. Found: 18.64.

A third sample was prepared and analyzed in the absence of air and moisture.

Anal. Subst., 0.6246; NH_3, 0.1159. Calcd for $GaI_3.6NH_3$; NH_3, 18.49. Found: 18.55.

Analyses were not made here for gallium and iodine since the samples of the triiodide were taken from a larger lot which had been carefully purified and analyzed (see ref. 11).

The increase in weight, as given in Table II, and the ammonia analyses show six molecules of ammonia in combination with one gram molecule of gallium triiodide. The ammonate was found to possess properties similar to those of the corresponding bromide salt.

II. Gallium Trifluoride Trihydrate and its Reaction with Ammonia

The third group elements boron, aluminium, indium and thallium are known in combination with fluorine. According to the literature, no attempts have been made to study the reactions of gallium with fluorine and fluorides. The present authors[11] observed that metallic gallium reacts readily with hydrofluoric acid (50% solution) to produce a white substance, insoluble in excess acid and of much greater volume than the original amount of metal. In the present investigation, this reaction has been studied in more detail to show that the product is a hydrated fluoride of gallium, $GaF_3.3H_2O$. This hydrated salt is also studied in the liquid ammonia solution.

Gallium Trifluoride Trihydrate.

The hydrated salt was prepared by two methods, namely, (A) by a reaction of metallic gallium with hydrofluoric acid (50% solution)and (B) by a reaction between gallic oxide and hydrofluoric acid (50% solution).

(A). A small amount of metallic gallium was treated with hydrofluoric acid in a platinum crucible. Reaction followed immediately to produce a white substance which appeared to be insoluble in the acid. The reaction was hastened considerably by making contact between the metallic gallium and the crucible with a piece of platinum wire. After the reaction was allowed to proceed in this manner for several hours, the excess acid was removed by evaporation over a steam bath. The increase in weight of the product over that of the metal suggests the formation of $GaF_3.3H_2O$ as is shown in the following table.

In each case the actual yield of the product was slightly less than that calculated for $GaF_3.3H_2O$. It was noticed, however, that during the reaction and the evaporation of the excess acid, a small amount of the solution was carried out of the crucible in the spray of escaping hydrogen and hydrogen fluoride.

TABLE III

Preparation of Gallium Trifluoride Trihydrate

Weight of gallium, grams	Weight of salt obtained, grams	Weight calc. for $GaF_3.3H_2O$.
0.4858	1.2347	1.2590
0.8155	2.0644	2.1149
0.5418	1.3933	1.4055

Analysis. Two samples of the salt, each from a different preparation, were analyzed for gallium and fluorine. For the gallium analysis, the salt was dissolved in dilute hydrochloric acid, gallium hydroxide was precipitated with ammonium acid sulfite,[12] and the hydroxide was ignited and finally weighed as gallic oxide.

Anal. Subst., 0.2239, 0.2959; Ga_2O_3, 0.1160, 0.1539. Calcd. for $GaF_3.3H_2O$; Ga, 38.57. Found: 38.54, 38.69.

For the fluorine analysis, the method of Starck and Thorin[13] was used with slight modification.[14] The fluorine was precipitated as calcium fluoride which was found to be exceedingly difficult to filter on account of its gelatinous structure. Accordingly, the calcium fluoride was precipitated and weighed with a known amount of calcium oxalate. A weighed quantity of sodium oxalate was added to the solution slightly acidified with acetic acid; to this solution was added an excess of calcium chloride. The precipitate was dried at 210° and the weight of calcium oxalate was deducted to give that of the calcium fluoride.

Anal. Subst., 0.3325, 0.2269; CaF_2, 0.2152, 0.1483. Calcd. for $GaF_3.3H_2O$; F, 31.53. Found: 31.51, 31.82.

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[12] Porter and Browning: J. Am. Chem. Soc., 41, 1491 (1919).

[13] Starck and Thorin: Z. anal. Chem., 51, 14 (1912).

[14] Sodium oxalate was substituted for oxalic acid.

(B). A more convenient method of preparation of the hydrated fluoride was found in the treatment of gallic oxide with hydrofluoric acid (50% solution).[15] The oxide is readily soluble in this acid solution. When the excess acid is removed by evaporation, $GaF_3.3H_2O$ is obtained as a fine white powder. The results of this reaction are given in Table IV; the analyses are recorded below.

TABLE IV

Preparation of Gallium Trifluoride Trihydrate

Weight of Ga_2O_3, grams	Weight of salt obtained, grams	Weight calc. for $GaF_3.3H_2O$, gram
0.1986	0.3756	0.3829
0.4019	0.7728	0.7749
0.3066	0.5875	0.5912

Anal. Subst., 0.5875, 0.5799. Ga_2O_3, 0.3066, 0.3003. Calcd. for $GaF_3.3H_2O$; Ga, 38.57. Found: 38.83, 38.53.

Properties. Gallium trifluoride trihydrate is a fine white powder as prepared by the above described methods, insoluble in cold water but appreciably soluble in hot water. It is readily soluble in dilute hydrochloric acid and sparingly soluble in hydrofluoric acid (50% solution). It is stable in air; a sample exposed to the atmosphere for several weeks showed no change in appearance or weight. When heated to 140° in a vacuum under the influence of an oil pump and Hg-vapor pump, water is slowly liberated. One-half of the water (1.5 mols) appears to be liberated much more easily than the remaining water molecules.[16]

The Action of Ammonia on Gallium Trifluoride Trihydrate. The hydrated fluoride was treated with liquid ammonia in a weighed, evacuated tube in a manner analogous to that employed in the preparation of the gallium bromide and gallium iodide ammonates. The system was evacuated to constant weight at room temperature. A white powder similar in appearance to the original salt resulted. The product was analyzed for ammonia and gallium according to the usual procedures which have already been described.

Anal. Subst., 0.3341, 0.0872; NH_3, 0.0476, 0.0122. Calcd. for $GaF_3.3/2H_2O.3/2NH_3$; NH_3, 14.23. Found: 14.25, 14.02.

Anal. Subst., 0.0853, 0.0825; Ga_2O_3, 0.0445, 0.0432. Calcd. for $GaF_3.3/2H_2O.3/2NH_3$; Ga, 38.84. Found: 38.81, 38.95.

The analyses suggest strongly that half of the water of the trihydrate is replaced by ammonia molecules. This result is in accord with the fact that half of the water of the trihydrate is easily removed when the salt is subjected to a high vacuum at 140°, while the remaining water molecules are removed with great difficulty at this temperature under the same conditions. The results merely suggest the empirical formula given above as one possibility since the molecular weight of the complex is not known.

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[15] Observations by Mr. M. C. Crew.

[16] Observations by Mr. M. C. Crew. The details of the dehydration of $GaF_3.3H_2O$ will appear in a later paper on the preparation of anhydrous gallic fluoride.

The addition of ammonia to the anhydrous gallic fluoride might produce results of an entirely different nature. Studies are now being made in this direction.

Summary

Gallium tribromide and gallium triiodide react with liquid ammonia at $-33.5°$ to form ammonates in which six molecules of ammonia are combined with the halide. The ammonates are stable at room temperature in the absence of moisture. It is shown that ammonia is readily displaced by water molecules when the ammonates are exposed to air. This process is found to be readily reversed in liquid ammonia.

The halides of gallium resemble those of indium and aluminium in their behavior with ammonia.

Two methods are given for the preparation of gallium trifluoride trihydrate.

The hydrated trifluoride is studied in liquid ammonia solution. A complex is formed in which one-half of the water is replaced by ammonia molecules.

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THE DIFFUSION OF GASES THROUGH FUSED QUARTZ

BY LIU SHENG T'SAI AND T. R. HOGNESS

In 1900 Villard[1] first observed that fused quartz, when heated to redness, was permeable to hydrogen. This observation was followed by a number of investigations[2-13] on the diffusion of hydrogen, helium, neon, argon, oxygen, and nitrogen through fused silica and through various kinds of glass. Quantitative measurements of permeabilities for gases other than hydrogen and helium have not been made, and some of the qualitative observations are in disagreement.

Williams and Ferguson[9] found that with gas pressures up to one atmosphere, and temperature to 881°C no leakage of air or nitrogen gas through silica glass was observed. Berthelot observed that both oxygen and nitrogen were present in an evacuated tube after heating in air for half an hour at 1300°C., while Wustner[7] found that nitrogen diffused through quartz at 900°C and 1,000 atmospheres, and that under approximately the same conditions, oxygen did not. Mayer's[6] observations showed that for pressures smaller than atmospheric neither oxygen nor nitrogen diffused through quartz, while for pressures greater than atmospheric this experimenter found an increase in diffusion with increase in pressure and temperature.

Williams and Ferguson and Van Voorhis also found that the silica glass is permeable to helium, and is easily observable at 180°C. The permeability is proportional to gas pressure, and, according to the former of these observers, is an exponential function of the temperature.

Richardson and Richardson[4] observed that neon diffused through quartz at about 1000°C. After one hour's heating in air a faint blue argon spectrum and a yellow helium line were obtained, while prolonged heating resulted in the more fully developed spectra of both helium and neon. The argon spectrum, they concluded, was due to the trace of air absorbed by the wall of the tube before heating.

In preparation for later experiments it was found desirable to have better data on the permeability of quartz glass for some of these gases, so we have undertaken quantitative determinations of this property.

Apparatus and Experimental Procedure

The diffusion cell consisted of a thin tube of clear fused quartz, the thickness of which was measured by three different methods: (1) measurement with calipers, (2) calculation of the thickness from the weight of water displaced by the quartz tube, the density and the area of the immersed portion of the quartz tube being known, (3) by the same method as (2) except that mercury was used instead of water. The average of these measurements gave a thickness of 0.033 cm. After the thickness had been determined the tube was sealed off at one end and at the other end it was sealed to a quartz capillary which was in turn connected to the McLeod gauge through a quartz-pyrex graded seal. Around the cell, which had the dimensions of 1.46 cm outside diameter by 16 cm, a heavy-wall quartz test tube was fitted to hold the gas. To ensure the air-tightness of the necessary glass-rubber connection, which was of such length that it was far away from the furnace, DeKhotinsky cement was used. In addition, an electric fan was used to facilitate the cooling.

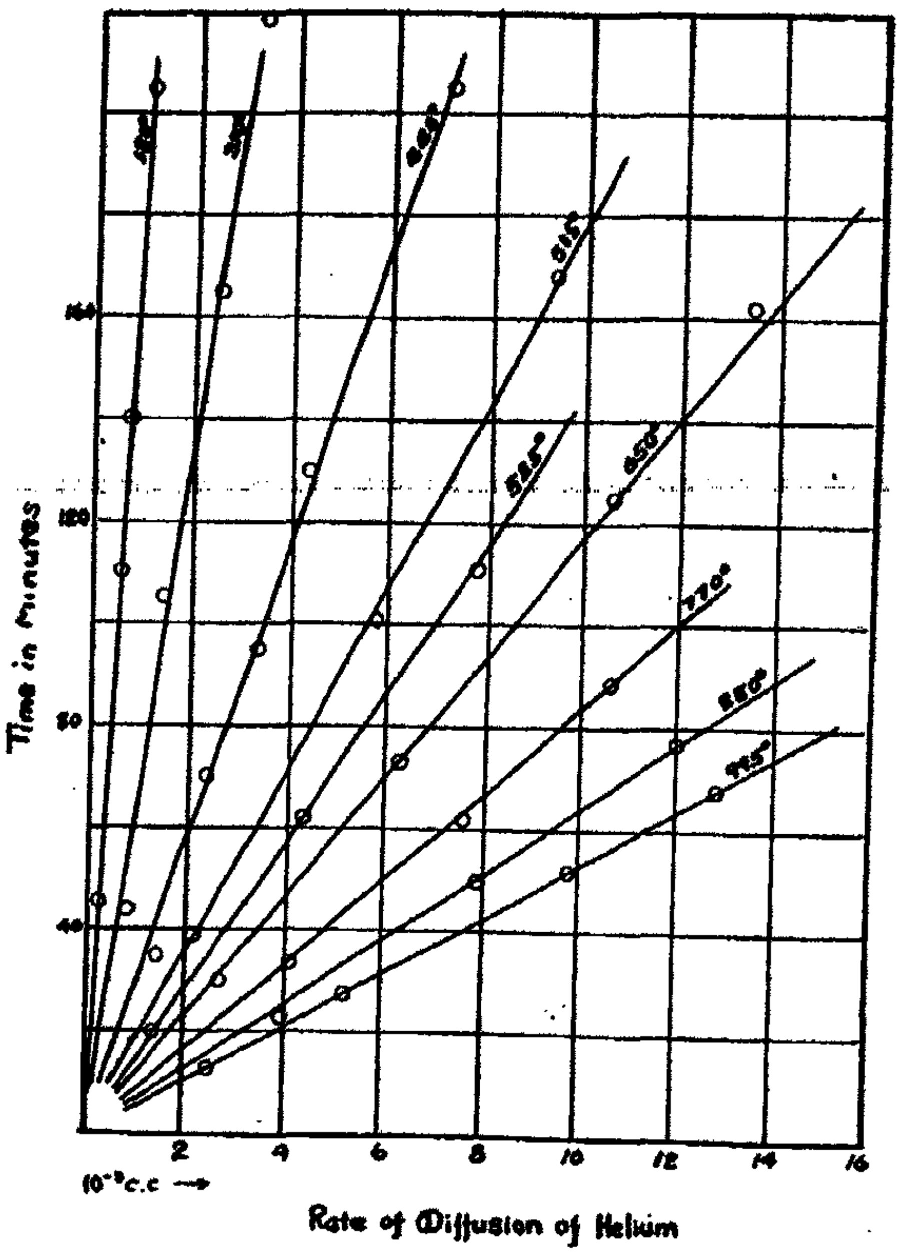

FIG. 1

After the apparatus was set up the whole system was evacuated for about three days. At the end of this time the pressure in the apparatus was less than 1×10^{-5} mm but on standing for about twelve hours the pressure increased to about 2×10^{-4} mm. The casing was then evacuated and the gas in question was introduced. The system was evacuated during the time that it took for the furnace to reach temperature equilibrium, about three hours, after which time the pump was disconnected and the measurements were begun. The increase in pressure was determined with a McLeod gauge at regular intervals of time, and such results as were obtained for neon and helium are shown in Figs. 1 and 2. As has been noted, there was a slight increase of pressure with time due to the desorption of the gas from the glass walls. It was, therefore, necessary to make this correction for the gases which diffuse rather slowly. This was done by noting the rate of increase of pressure of the system while the cell was at the temperature under investigation and the casing evacuated. The difference between the apparent rate obtained in the usual manner, and this blank rate gave the actual rate due to diffusion. When these corrections were taken into consideration no definite diffusions were observed for nitrogen, oxygen, and argon. In the case of argon, spectroscopic tests showed that diffusion of this gas took place at the highest temperatures, but that the rate was not enough to offer any quantitative data.

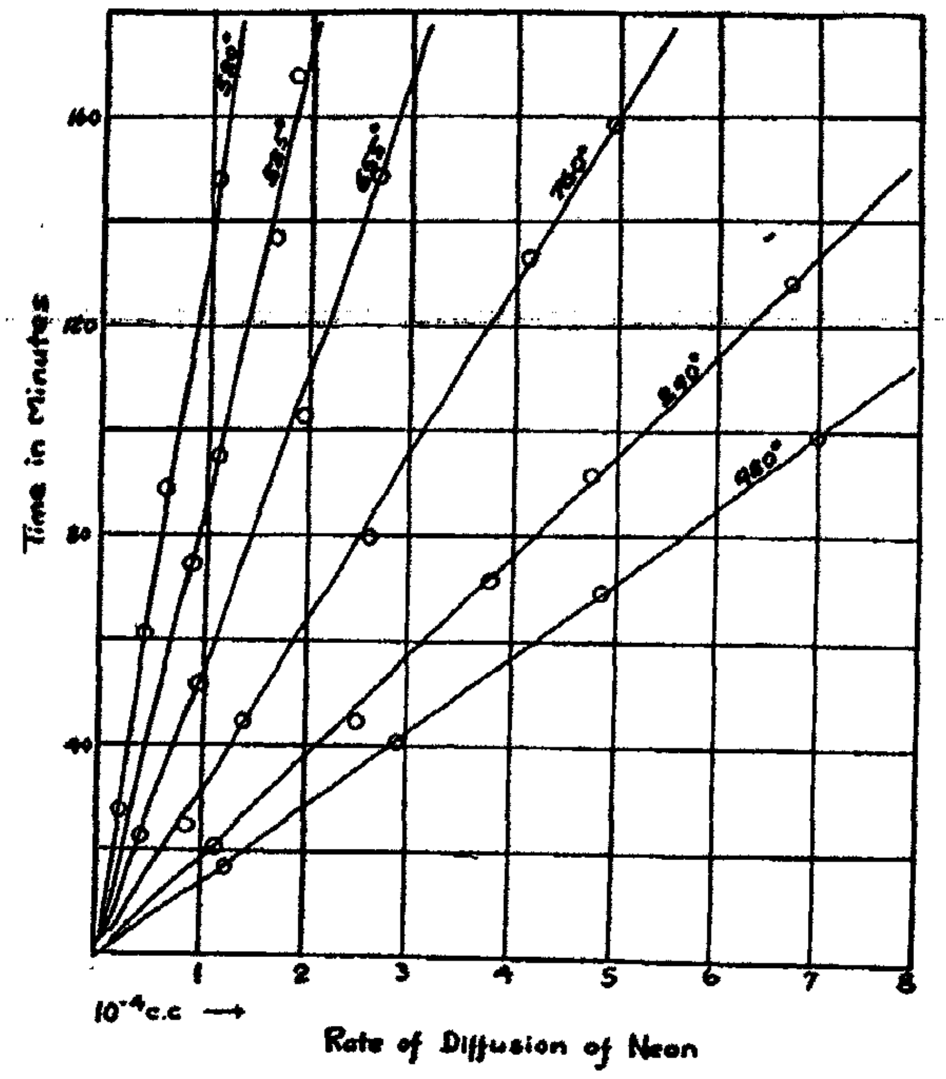

FIG. 2

Preparation of Materials

Helium was supplied in a pure form by the United States Bureau of Mines, and was used without further purification.

Neon, supplied by the Air Reduction Company, was purified three times by fractional condensation with activated charcoal at liquid air temperature. Any helium present in the original neon was removed in this way.

Argon, supplied by the same company, was used without purification.

Oxygen was prepared by heating potassium chlorate and manganese dioxide. The gas was led through a phosphorus pentoxide tube before using.

Nitrogen was prepared by heating a solution of sodium nitrite and ammonium chloride. The gas was purified by passing it through a tube containing dry potassium hydroxide and then over phosphorus pentoxide.

Discussion of Results

Permeability is here defined as the rate in cubic centimeters (measured at 0°C and 760 mm) per hour at which the gas at one atmosphere pressure diffuses into vacuum through a wall 1 mm thick and 1 square centimeter in area. Table I shows the permeability of quartz glass for both helium and neon at different temperatures. The calculation of these values was made by assuming that the rate of diffusion is inversely proportional to the thickness of the wall, an assumption which, according to the mathematical formulation of the simple theory of diffusion, is a valid one for thin walls.[7] The plot of the logarithms of the permeability against temperature for these two gases is shown in Fig. 3.

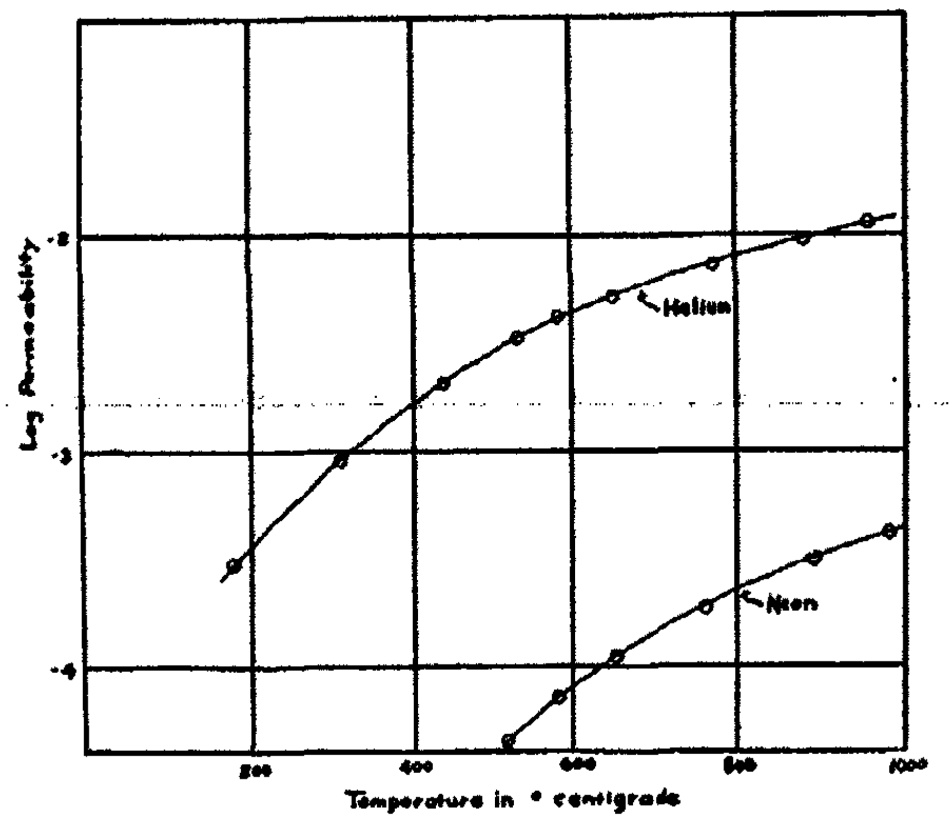

Fig 3

In as much as the permeability of glass increases very rapidly with the temperature, it has been assumed that this function is an exponential one. Williams and Ferguson, from measurements at three temperatures, concluded that in the case of helium such an exponential relationship existed. More observations, however, were necessary to indicate the real trend of the curve. Our results show that the increase in permeability with temperature is somewhat less than that which the exponential relationship demands. For the permeability of helium at 440° and at atmospheric pressure, Williams and Ferguson obtained a value of 39×10^{-4} cc, Van Voorhis, approximately 25×10^{-4} cc, while we get a value of 21×10^{-4} cc. As shown by these authors, different samples of silica glass gave different values of the permeability for hydrogen, so we do not expect a better check than this. The permeabilities for helium and neon at 900°C and atmospheric pressure are 100×10^{-4} and 3.2×10^{-4}, or in the ratio 31 to 1, respectively. Williams and Ferguson found a ratio of 22 to 1 for helium and hydrogen at 500°C and 760 mm.

TABLE I

Permeability for Helium

Temperature	Permeability × 10^4	Log Permeability
180°C	3	−3.523
310	9	−3.046
440	21	−2.678
535	33	−2.482
585	42	−2.377
650	51	−2.293
770	72	−2.143
880	94	−2.027
955	113	−1.947

Permeability for Neon

Temperature	Permeability × 10^4	Log Permeability
520°C	.45	−4.347
585	.70	−4.155
655	1.10	−3.959
760	1.85	−3.733
890	3.15	−3.502
980	4.20	−3.377

If the increasing permeability with increasing temperature were due solely to the increased velocity of the permeating molecules one would expect the permeability to increase as the square root of the temperature. This is very far from the case. The quartz glass must be regarded as possessing channels[14] which increase in clearance with increasing temperature. As shown by X-ray analysis,[15] silica glass, when heated for thirty minutes at 700°C, undergoes marked devitrification. This undoubtedly increases the channels for the diffusing gas, increasing the permeability. We found that silica glass, when heated to high temperatures, undergoes a permanent change which results in a noticably greater permeability for helium. Since different samples of quartz glass give slightly different results, and since the permeability depends somewhat upon the previous heat treatment of the glass, the absolute values we give here are for one particular sample only, and cannot be applied too exactly in other calculations.

As one would expect, the permeability of quartz glass for various gases is greater for the atoms or molecules of smaller cross section. Our positive result for argon is undoubtedly real but the value of the permeability of quartz for this gas was so low that its measurement was impossible. The heavier rare gases would undoubtedly diffuse so slowly as to prohibit detection, if any diffusion at all took place.

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METHANE EQUILIBRIA FROM ABSOLUTE ENTROPIES, WITH A NOTE ON THE USE OF THE EHRENFEST SYMMETRY NUMBER

BY A. R. GORDON AND COLIN BARNES

The entropy of methane at 298°K was calculated from spectroscopic data by Giauque, Blue and Overstreet[1] who used the Ehrenfest formula which is strictly valid for the rotational entropy at this temperature. A calculation by Villars,[2] using the rotational symmetry characters of Elert,[3] gave the same result when corrected for some numerical errors.[4] The value so obtained for the entropy agreed moderately well with the free energy data derived by Storch[5] from the measurements made by Randall and his associates on the two reactions

$$CH_4 + 2\,H_2O = CO_2 + 4\,H_2 \tag{I}$$

$$C_{(Graph)} + 2\,H_2 = CH_4 \tag{II}$$

The calculations of Storch, however, involved specific heats which are not in agreement with those calculated from the vibration spectrum of methane. A consistent computation, using spectroscopic entropies and heat capacities of the gases, may now be carried out for these reactions; the only other quantities that are involved are the "third law" entropy of graphite and the calorimetric values of the heats of reaction.

1. The Entropy of Methane from 300° to 1200°K

In the calculations mentioned above, only a single temperature was considered; for the present purpose it is necessary to compute the entropy of methane up to 1200° in order to cover the equilibrium data on reactions I and II.

The molar translational entropy for temperature T and pressure 1 atmosphere for a gas of molecular weight M (= 16.036) is given by the usual Sackur-Tetrode formula[6]

$$S_T = -\,2.295 + 3R/2.\ln M + 5R/2.\ln T \tag{1}$$

The values of this expression for the various temperatures are entered in Table I.

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[1] Giauque, Blue and Overstreet: Phys. Rev., (2) 38, 196 (1931).

[2] Villars: Phys. Rev., (2) 38, 1552 (1931).

[3] Elert: Z. Physik, 51, 6 (1928).

[4] MacDougall: Phys. Rev., (2) 38, 2074 (1931).

[5] Storch: J. Am. Chem. Soc., 53, 1266 (1931).

[6] The values of the constants used are (Handbuch der Physik, 1926): R = 1.9858 cals./deg.; k = 1.372×10^{-16} ergs/deg.; h = 6.55×10^{-27} erg. sec.; N = 6.06×10^{23}; 1 atmos. = 1.0133×10^{6} dynes/cm².

The methane molecule, considered as a completely symmetrical rigid rotator, has three equal moments of inertia $A = B = C = 5.17 \times 10^{-40}$, given by the measurements of Dickinson, Dillon and Rasetti[1] on the Raman effect in methane; if I be written for $\sqrt[3]{ABC}$, such a model gives a classical rotational entropy

$$S_R' = 3R/2 + 3R/2.\ln 8\pi^{7/3}IkT/h^2 \qquad (2)$$

when *all* the rotational levels are taken into account. From the work of Elert,[2] however, it is known that only one-twelfth of the rotational states in methane are to be retained, for this is the fraction of all the molecular states which belong to a definite symmetry class, either completely symmetrical or completely antisymmetrical. For temperatures ranging from 300° to 1200°, the state sum (see note on symmetry number below) for the rotational entropy is just 1/12 of the value used in the derivation of S'_R; i.e. if S'_R is to be retained, we must subtract R ln 12 from it to get the value of the rotational entropy of methane. This is, of course, what is meant by saying that the CH_4 molecule has a "symmetry number" 12.

The weight g of the lowest electronic configuration is 1 and will not enter into the complete expression for the entropy. The four hydrogen atoms in the methane molecule (for the temperature range considered) contribute, due to their intrinsic spins, an entropy 4R ln 2; thus the quantity S_R, entered for various temperatures in Table I, is given by

$$S_R = S_R' - R \ln 12 + 4R \ln 2 \qquad (3)$$

The fundamental vibration frequencies have been given by Dennison;[3] they are

4217 (1) 1520 (2) 3014 (3) 1304 (3)

in cm^{-1}, where the number in brackets after a frequency indicates its degree of degeneracy, i.e. the number of times it must be supposed to occur in calculating the state sum for the vibrational entropy S_V. S_V, computed in the usual way, is entered in Table I for the various temperatures. The total entropy is given by

$$S = S_T + S_R' + S_V - R \ln 12 + 4R \ln 2 = S_T + S_R + S_V \qquad (4)$$

and is entered in Table I. The table also contains values of the heat capacity of methane at constant pressure for the temperatures considered; the vibrational contributions were computed from the fundamental frequencies of the molecule in the usual manner.

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[1] Dickinson, Dillon and Rasetti: Phys. Rev., (2) 34, 582 (1929).

[2] Elert: Loc. cit.

[3] Dennison: Astrophys. J., 62, 84 (1925); Dennison and Ingram: Phys. Rev., (2) 36, 1451 (1930).

TABLE I

Molar Entropy and Heat Capacity at Constant Pressure(1 atmos) of Methane

T°K.	S_T	S_R	S_V	S	C_P
300	34.288	15.612	0.108	50.01	8.54
400	35.716	16.469	0.429	52.61	9.71
500	36.824	17.134	0.971	54.93	11.09
600	37.729	17.677	1.666	57.07	12.46
700	38.494	18.136	2.458	59.09	13.71
800	39.157	18.534	3.301	60.99	14.87
900	39.742	18.884	4.181	62.81	15.90
1000	40.265	19.198	5.066	64.53	16.83
1100	40.738	19.482	5.954	66.17	17.67
1200	41.170	19.741	6.833	67.74	18.45

2. The Equilibrium I

If P_X is the partial pressure of a component X in this reaction and if K be defined by

$$K = P_{CH_4}.(P_{H_2O})^2/P_{CO_2}.(P_{H_2})^4$$

then

$$R \ln K = -Q/T + \Sigma S \tag{5}$$

where Q is the heat of reaction at temperature T and

$$\Sigma S = S_{CH_4} + 2S_{H_2O}(g) - S_{CO_2} - 4S_{H_2}$$

the entropies being all for temperature T and pressure 1 atmosphere.

The heat of combustion of methane[1] at 298° is 212790 cals., and the heat of formation of water[1] at the same temperature is 68313 cals.; from these two numbers and the heat of vaporization[2] of water at this temperature (10485 cals.), $Q_{298} = -39500$ cals. The values of Q for higher temperatures can now be found by integration of the specific heat curves, the heat capacities for methane being given in Table I and the values for the other gases having been previously calculated.[3] The values of Q/T so obtained are given in Table II. Values of ΣS, obtained from the methane entropies in Table I and the known entropies of the other gases[3] are entered in Table II, which also gives the resulting values of R ln K. From the latter the curve in Fig. I was constructed.

TABLE II

The Equilibrium $CH_4 + 2\ H_2O = CO_2 + 4\ H_2$

T°K.	575	600	625	650	675	700
−Q/T	74.08	71.40	68.92	66.62	64.48	62.49
−ΣS	49.03	49.49	49.87	50.24	50.59	50.90
R ln K	25.05	21.91	19.05	16.38	13.89	11.59

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[1] Rossini: Bur. Standards J. Research, (6) 1, 36 (1931).

[2] Int. Crit. Tables, 5, 138.

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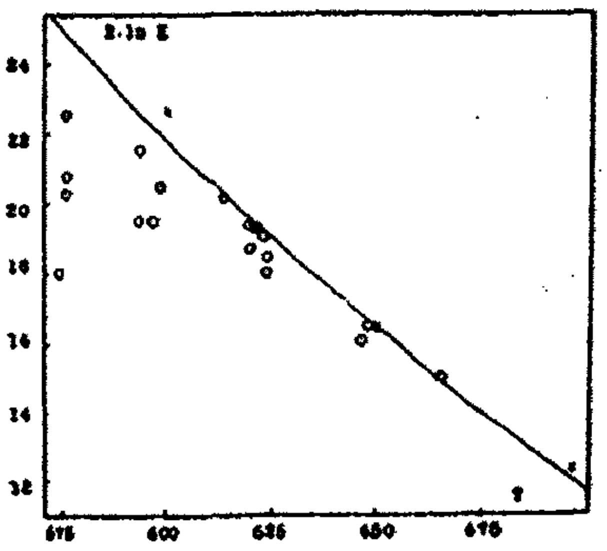

FIG. 1

The experimental numbers obtained by Randall and Gerard[1] for this reaction are shown in the same figure; the small circles indicate values obtained in approaching equilibrium from the $CO_2 - H_2$ side, and the crosses those obtained in approaching equilibrium from the $CH_4 - H_2O$ side. As is evident from the figure, the agreement between the calculated and observed values of R ln K is quite satisfactory; the use of spectroscopic entropies and specific heats has removed the discrepancy supposed to exist between the calculated and observed entropy change for the reaction. The values[2] suggested for this reaction are $-\Delta H^\circ_{298.1} = -39500$, $-\Delta S^\circ_{298.1} = -41.52$, $-\Delta F^\circ_{298.1} = -27120$.

3. The Equilibrium II

In this reaction the entropy of graphite gives rise to the most uncertainty, as there is always an element of risk when using a calorimetric entropy in conjunction with spectroscopic entropies. Fortunately an independent check is available here, since the equilibrium constant for the reaction

$$C_{(\text{Graph})} + CO_2 = 2\,CO$$

is fairly accurately known.[3] Using the equation of Magnus[4] for the heat capacity of graphite, and the value 1.22 calories per degree for the entropy of graphite[5] at 273.1°, the entropy for the three temperatures 1123°, 1173° and 1223° is found to be 6.47, 6.70 and 6.92, respectively. The entropies of carbon monoxide and and carbon dioxide can be found by interpolation from Gordon and Barnes' Tables IV and V,[6] giving −41.58, −41.47 and −41.35 as the values of $(S_{(\text{Graph.})} + S_{CO_2} - 2S_{CO})$ for the three temperatures. From the heat of combustion of graphite,[7] viz. 94420 cals. at 291°, and that of carbon monoxide[8] (67623 cals. at 298°), $Q_{298} = -40826$, so that Q/T for 1123°, 1173° and 1223° is −35.63, −34.00 and −32.50, respectively; hence, R ln $(P_{CO_2})/(P_{CO})^2$ for the three temperatures is −5.95, −7.47 and −8.85. The corresponding experimental numbers are −5.26, −7.47 and −8.54, in reasonably good agreement.

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[1] Randall and Gerard: Ind. Eng. Chem., **20**, 1335 (1928).

[2] The entropy of carbon dioxide at 300° is 51.09, not 51.19 as entered in Gordon and Barnes' Table V; the mistake arose from the value entered for S_V at this temperature; this should be 0.738, not 0.838 as printed.

[3] Rhead and Wheeler: J. Chem. Soc., **97**, 2178 (1910).

[4] Int. Crit. Tables, **5**, 94.

[5] Int. Crit. Tables, **5**, 87.

[6] Gordon and Barnes: Loc. cit.

[7] Roth and Wallasch: Z. Elektrochemie, **21**, 1 (1915); Roth: **26**, 288 (1920).

[8] Rossini: Loc. cit.

From the heats of combustion of methane and graphite, and the heat of formation of water, the heat of formation of methane at 298° is 18256 cals; from this and the heat capacities of graphite, methane (Table I) and hydrogen,[1] the values of Q/T entered in Table III are found by tabular integration. The entropies of methane (Table I), of hydrogen[1] and of graphite[2] lead to the values of $\Sigma S = S_{(\text{Graph.})} + 2S_{H_2} - S_{CH_4}$ entered in that table. The resulting values of $R \ln (P_{H_2})^2/(P_{CH_4})$ are shown by the curve in Fig. II.

TABLE III

The Equilibrium $C_{(\text{Graph.})} + 2H_2 = CH_4$

T°K	700	800	900	1000	1100	1200
Q/T	29.68	26.51	23.96	21.87	20.10	18.58
ΣS	24.88	25.47	25.90	26.21	26.45	26.63
R ln K	−4.80	−1.04	+1.94	+4.34	+6.35	+8.05

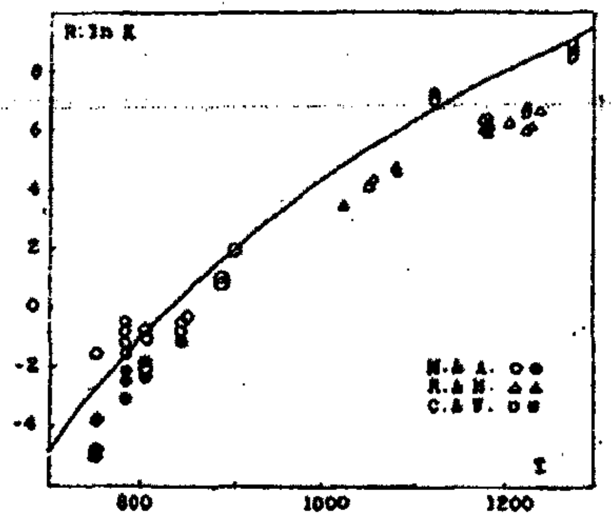

FIG. 2

The same figure shows the relation of the calculated curve to the experimental values obtained by Mayer and Altmayer,[3] by Randall and Mohammed[4] and by Coward and Wilson;[5] the forward reaction, i.e. methane synthesis, gives the points indicated by the light symbols; the reverse reaction gives those indicated by the black symbols. For the lower part of the temperature range the calculated curve lies satisfactorily with regard to the experimental points, but the agreement is not so close at higher temperatures where the experimental curve would lie about 1 cal./degree below that of the figure.

Villars[6] has recently suggested frequencies for the methane molecule somewhat different from those used above, but in better agreement with observed Raman lines; he replaces Dennison's single frequency 4217 cm^{-1} by the Raman frequency 2914.8 but leaves the other frequencies unchanged. This makes an appreciable difference in the entropy and heat capacity of methane[7] only for

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[1] Gordon and Barnes: Loc. cit.

[2] The graphite entropies were computed from the entropy at 273.1° by tabular integration of (Cp/T).dT; they are

T°K	700	800	900	1000	1100	1200
S	4.15	4.76	5.33	5.86	6.36	6.83

[3] Mayer and Altmayer: Ber., **40,** 2134.

[4] Randall and Mohammed: Ind. Eng. Chem., **21,** 1048 (1929).

[5] Coward and Wilson: J. Chem. Soc., **115,** 1380 (1919).

[6] Villars: Preprint of papers to be presented at the New Orleans meeting of the American Chemical Society, March 30, 1932, Paper No. 32.

[7] Using Villars' frequencies, the numbers are (cf. Table I):

T°K	700	800	900	1000	1100	1200
S	59.12	61.05	62.90	64.66	66.33	67.94
C_p	13.86	15.11	16.22	17.21	18.09	18.90

temperatures greater than 700°. As far as the calculation of R ln K for Reaction II is concerned, however, the changes introduced in Q/T and ΣS partly cancel, and thus the equilibrium constant is only slightly altered; the use of Villars' frequencies would change −1.04 for 800° into −1.05 and +8.05 for 1200° into +8.00, far too small a correction to account for the discrepancies shown in Fig. II.

The satisfactory agreement in the case of Reaction I would indicate that the quantities used in the calculations are not very seriously in error. A reasonable explanation for the drift in R ln K for Reaction II at the higher temperatures lies in the experimental conditions under which equilibrium was attained; side reactions leading to the formation of hydrocarbons other than methane undoubtedly occur,[1] particularly at high temperatures, and low values of K would result from the measured excess of methane. In view of the experimental difficulties on the one hand, and the uncertainties inherent in the calculation of a vibration-rotation entropy on the other, the agreement in this case also is probably as close as can be expected.

The value of $-\Delta F^\circ_{298.1}$ for methane,[2] calculated from the heat of formation and the entropies, is 12490 cal.

4. Note on the use of the "Symmetry Number"

From the work of Gibson and Heitler[3] and of Ludloff,[4] it is now known that the Ehrenfest symmetry number, σ, originally introduced as a geometrical concept into the classical phase space of a gas, is merely a convenient way of expressing what fraction of all the energy states of a molecule have a certain symmetry character; the expression "symmetry character" is to be understood in the sense of quantum mechanics as applied to molecules containing two or more identical nuclei. If the energy states ϵ_n of a molecule occur with the weight factors p_n, the familiar entropy expression is

$$S = R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \tag{6}$$

where Σ_1 (the state sum) and Σ_2 (the energy sum) are defined by

$$\Sigma_1 = \sum_n p_n.e^{-\epsilon_n/kT}; \qquad \Sigma_2 = \sum_n p_n.(\epsilon_n/kT).e^{-\epsilon_n/kT} \tag{7}$$

For temperatures above 300°K, the evaluation of these sums, for practically all types of molecules, leads to the classical expression for the rotational entropy, provided no states are rejected on a basis of selection of some definite type of symmetry. In the computation of such an entropy, however, we must select only those states of a certain symmetry; the correction to the classical expression is then summarized in a symmetry number. It appears that when no enumeration of the rotational symmetry characters can be made, no symmetry number can be deduced with certainty from an assumed geometrical

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[1] See Storch: Loc. cit.; Pring and Fairlie: J. Chem. Soc., **101**, 91 (1912).

[2] Giauque, Blue and Overstreet's value (loc. cit.) is 12440.

[3] Gibson and Heitler: Z. Physik, **49**, 465 (1928).

[4] Ludloff: Z. Physik, **57**, 227 (1929).

model; even in simple cases the geometrical concept can only be made to give the desired number by some device or other, which essentially involves a knowledge of the rotational characters themselves.

In the case of models of some exact geometrical figure, e.g. a regular tetrahedron, it is often possible from the wave equation of the molecule, to find the fraction of the rotational levels which are, say, symmetrical in the nuclei; this fraction is one-twelfth in methane, one-third in ammonia, and so on. But if the molecule only roughly approximated to a regular figure, it would then possess no symmetry number suggested by geometry. A small continuous deformation of the regular figure will change its moments of inertia continuously, and it is known that the rotational energy values are continuous functions of the moments of inertia, so that the energy values will themselves change continuously; for example, if the deformation of a symmetrical methane molecule (three equal moments of inertia $A = B = C$) be such that A, B and C are no longer equal, the $(2J + 1)$[1] originally coincident rotational levels for a given J will proceed to separate under the deformation into $(2J + 1)$ distinct levels each $(2J + 1)$—fold degenerate. Now the symmetry character of a level (and therefore its weight) is invariant for a deformation of the molecule; thus Hund[2] used the deformation of a symmetrical top to establish the symmetry characters for an unsymmetrical rotator; hence the entropy given by Eq. 6 must be a continuous function of the moments of inertia, and must only change slightly as a result of a small deformation. All geometric symmetry has by now been lost, however, and no symmetry number in the Ehrenfest sense can be assigned. Of course, when one keeps in mind the quantum significance of σ, this difficulty vanishes; the fraction of states of given symmetry character will be conserved for small deformations from geometric symmetry, and it would still be necessary in Eq. 3 to use $\sigma = 12$ for a methane molecule which need only roughly approximate to a regular tetrahedron.

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[1] Giauque, Blue and Overstreet: Loc. cit.

[2] Hund: Z. Physik, **43**, 822 (1927). To be precise, permissible deformations must result from perturbations symmetrical in the like particles.

The necessity for the invariance of the symmetry characters during a deformation is evident when one considers the question of nuclear spin. With four hydrogen nuclei in the molecule, Villars (loc. cit.) has shown that there are five S(4) spin wave functions, three S(3+1) each threefold degenerate, and one doubly degenerate S(2+2)—sixteen in all. From the work of Elert (loc. cit.) one twelfth of the rotational states in methane are S(4), nine twelfths are S(3+1) and two twelfths are S(2+2). If Σ is the value of the State Sum in the absence of symmetry and spin (see Eq. 2), then its high temperature value (to a close approximation) in the presence of symmetry and spin will be

$$5 \times \Sigma/12 + 9 \times 1/9 \times \Sigma/12 + 2 \times (1/4 + 1/4) \times 2\Sigma/12 = 16\Sigma/12$$

(The factors 1/9 and (1/4 + 1/4) arise from the fact that only one ninth of the products of two S(3+1) functions are S(4), while one quarter of the products of two S(2+2) are S(4) and one quarter A(4) both of which may be retained owing to the double character of the ground vibrational state). It is for this reason that the classical formula gives the rotational entropy of methane correctly if the classical expression is corrected by a symmetry term —R ln 12 and a spin term +R ln 16. That the spin contribution is just R ln 16 is in conformity with the rule that at high temperatures spin entropy must cancel in the entropy of reaction.

Since the spin wave functions are independent of the geometrical arrangement of the particles, it is necessary that the rotational symmetries be unaltered during the deformation, since otherwise the spin contribution would no longer be R ln 16.

In Cooley's measurements[1] on the infra red adsorption spectrum of methane, different fine structure separations are found for the bands 3.31 μ and 7.7 μ, corresponding to the existence of at least two different moments of inertia; this result is of course quite incompatible with a regular tetrahedral structure. Asymmetry is also indicated by the work of Langseth[2] on the Raman effect in carbon tetrachloride and carbon tetrabromide. If it should prove that only two of the methane moments of inertia are equal to 5.17×10^{-40}, while the third is, say, ten per cent larger, the rotational entropy given by Eq. 3 would be only 0.1 cals./degree greater than that entered in Table I, the symmetry number 12 being retained in accordance with the preceding argument. Conversely, if the use of a given symmetry number leads to an entropy in approximate agreement with experiment, this must not be used as evidence as to the exact "shape" of the molecule.

The use of the symmetry number, where geometrical symmetry is excluded, is illustrated by the following simple calculation:

(*a*) Consider an unsymmetrical pyramidal molecule RX_3 whose moments of inertia are such that $(h^2/8\pi^2kT).(1/A,1/B,1/C) = 0.10, 0.09, 0.08$; the energy levels can then be found from the equations for an unsymmetrical rotator. Assume that the three X nuclei have no spin and are slightly different, e.g. three different isotopes. Then the weight factor for each of the $2J + 1$ rotational levels for a given J is simply $2J + 1$ since symmetry considerations are entirely excluded. The values of the energy and state sums are entered in the column *a* of the table below, together with the resulting value of the entropy obtained from Eq. 6; the expression S_R' (Eq. 2) is here applicable without correcting terms.

(*b*) If the three X nuclei are identical but non-spinning, then from a consideration of the limiting case as $A \rightarrow B < C$, for a given J the levels $\tau = J, J\text{-}5, J\text{-}6, J\text{-}11, J\text{-}12, \ldots$ will be either symmetrical or antisymmetrical in the X nuclei, while for other values of τ the levels will have degenerate symmetry; thus since the lowest vibrational state is double, having both a completely symmetric and a completely antisymmetric character, the levels $\tau = J, J\text{-}5, J\text{-}6, \ldots$ will have the weight $2J + 1$, the other levels having the weight zero. If Eq. 2 is to be used, a term $R \ln 3$ $(= 2.182)$ must be subtracted from the value of S_R' for case *a*, for the fraction one-sixth of the rotational levels can be associated with one of the lowest vibration symmetries, and a further fraction one-sixth with the second of the lowest vibration symmetries, so that one-third of the rotational-vibrational states are of a definite symmetry character.

(*c*) Finally, let each of the three X nuclei have one half unit of spin; the weights[3] of the levels $\tau = J, J\text{-}5, J\text{-}6, \ldots$ are then $4(2J + 1)$, the other levels receive the weights $2(2J + 1)$. If Eq. 2 is to be used, $-R \ln 3 + 3R \ln 2$ $(= 1.947)$ must be added to the expression on its right.

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[1] Cooley: Astrophys. J., 62, 73 (1925).

[2] Langseth: Z. Physik, 72, 350 (1931).

[3] Villars: Loc. cit., Table II.

	(a)	(b)	(c)
Σ_1	67.54	22.43	179.93
Σ_2	99.82	33.21	266.06
S_R (Eq. 6)	11.301	9.117	13.247
S_R (Eq. 2) corrected.	11.301	9.119	13.248

The table shews clearly that the rotational entropy, calculated by the classical Eq. 2, agrees with that obtained by evaluating the exact sums, when the classical expression receives the necessary corrections in the form of a symmetry number and a spin term. The table also shews that geometrical symmetry is a sufficient but not necessary condition for the existence of a symmetry number. It must be remembered, however, that the use of the classical formula for the rotational entropy, quite apart from corrections due to spin or to symmetry properties, is restricted to temperatures high enough for almost complete classical "excitation" of the rotational degrees of freedom. At lower temperatures the accurate summation formula must necessarily be used.

The University of Toronto,
Toronto, Canada.
April, 1932.

THE ROTATION OF ROCHELLE SALT IN ALKALINE MEDIA

BY ALAN NEWTON CAMPBELL AND ALEXANDRA JEAN ROBSON CAMPBELL

Introduction

In connection with work at present being carried out in this laboratory on the kinetics of racemisation, it was found necessary to determine the rotation of Rochelle salt in different strengths of NaOH. It was found that the specific rotation is very variable with alkali concentration and even changes sign at an alkali concentration of about 9 N.[1] Independent evidence was also furnished from determinations of OH′ concentration in these solutions, of complex formation. That the variation of rotation in different media is a consequence of loose complex formation loading the molecule is no new hypothesis, although the experimental evidence in favour of this assumption is practically non-existent. It seemed to us that in the case of Rochelle salt in NaOH the variation was so large that definite experimental evidence in favour of complex formation might be obtained. We have therefore applied the following independent methods to the problem:

1. Determination of OH′ concentration in sodium hydroxide solutions containing Rochelle salt.
2. Phase rule study of the system NaOH – $NaKC_4H_4O_6$. – H_2O.
3. Conductometric measurements.

The result has been to supply definite experimental evidence of complex formation.

Experimental

Mallinckrodt's U.S.P. Rochelle salt, $NaKC_4H_4O_6.4\ H_2O$ and stick caustic soda were used in the preparation of all solutions. Solutions of sodium hydroxide were prepared by dissolving stick NaOH in water. Repeated analysis showed these solutions to contain only the merest trace of carbonate. Solutions, for all but the phase rule measurements, were always made by dissolving one-tenth of a mol of hydrated Rochelle salt in the appropriate NaOH, and making up to 100 c.cs. The use of hydrated Rochelle salt reduces the alkalinity of each solution by 7.5%, but the figures given everywhere refer to the original strength of the NaOH.

Specific Rotations of Molar Rochelle Salt in Sodium Hydroxide of Various Concentrations. The determinations of rotation were carried out in a Hilger 3-field instrument, using a 2 dm. tube. In the absence of a monochromator we were obliged to use a series of light filters, which, however, gave perfect matching of the fields. The filters were Wallace colour filters, having the following transmissions:

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[1] Nature, 129, 281 (1932).

Filter No.	Transmission (Å)	Arithmetic Mean
2	7608–6100	6854
3	7608–5800	6704
4	7608–5400	6504
5	7608–5300	6454
6	7608–5000	6304

Needless to say, the arithmetic means are not the optical means, so that the figures for specific rotation have not an absolute significance. The temperature of measurement was 22.2° throughout. The results obtained are shown in Table I.

TABLE I

Specific Rotations

Normality of NaOH	Filter Number				
	2	3	4	5	6
Pure Water	+25.2	+26.8	+28.1	+28.5	+28.5
1.10	+23.3	+25.2	+26.3	+26.8	+27.1
1.907	+21.7	+22.9	+24.0	+24.4	+24.5
2.72	+19.7	+20.8	+21.7	+22.1	+22.1
5.16	+13.1	+13.7	+14.4	+14.8	+14.9
6.97	+ 6.68	+ 6.99	+ 7.2	+ 7.4	+ 7.5
9.36	− 0.43	− 0.91	− 1.12	− 1.22	− 1.26
14.18	−10.9	−12.0	−12.7	−12.7	−12.8

The negative rotations were quite stable in the cold, showing that no racemisation takes place in the cold.

Determination of OH' Concentration

Despite every precaution to purify the hydrogen, etc., the hydrogen electrode gave wavering and uncertain results in strongly alkaline solutions of Rochelle salt. Measurements based on the velocity of saponification of ethyl acetate were a little steadier but failed at high concentrations, owing to the increasing insolubility of ethyl acetate in strong alkali. It is well known that the quinhydrone electrode cannot be used in alkaline media. Perhaps the most satisfactory electrode turned out to be the manganese hydroxide electrode: this at least gave good comparative readings. All these measurements gave values for the OH' concentration lower in the solutions containing Rochelle salt than in the corresponding alkali alone, and indeed it was this which first led us to postulate complex formation. Nevertheless, we do not attach more than qualitative significance to the figures, which are given in Table II.

Conductometric Measurements. These were carried out by determining the molecular conductivity of the NaOH and molar Rochelle salt separately and then in mixed solutions. Simple additivity is not to be expected, but, according to the literature, the ionisation (or activity) of strong electrolytes

TABLE II

Concentration of NaOH	(OH) in NaOH alone	(OH) in NaOH R.S.	Method
1.10 N	0.775 N	0.117 N	Hydrogen Electrode
2.05 N	1.35 N	0.73 N	" "
2.03 N	—	0.41 N	" "
1.907 N	—	0.325 N	" "
1.07 N	—	0.103 N	" "
2.93 N	1.965 N	1.3 N	" "
1.1 N	—	0.147 N	Saponification of
1.9 N	—	0.81 N	Ethyl Acetate
2.95 N	—	0.78 N	" "
14.18 N	2.10 N	2.10 N	Manganese Hydroxide
9.36 N	2.817 N	1.75 N	Electrode

is not greatly affected by the presence of a second electrolyte with a common ion. However, a comparison experiment with mixed sodium and potassium chlorides was carried out. In similar work which is now being carried out with mandelic acid, and where it appears that complex formation, if it occurs at all, is only slight, the sodium hydroxide and mandelic acid reduce each other's conductivity only slightly.

No special precautions were taken, as this was not in itself a conductometric investigation, beyond placing the conductivity cell in a thermostat at 27.3°. The conductivity vessel was chosen to have a large cell constant (10.4) to prevent unduly high conductivities. The results are contained in Table III.

TABLE III

Substance and Concentration	μ obs.	Sum of μ of constituents	Diff.	Ratio
M/1 Rochelle Salt in Water	98	—	—	—
0.935 N NaOH	202	—	—	—
M/1 R.S. + 0.935 N NaOH	210	$202+\frac{(98\times 1000)}{935}=306.5$	96.5	0.685
1.97 N NaOH	164	—	—	—
1.97 N NaOH + M/1 R.S.	124	214	90	0.58
2.72 N NaOH	158	—	—	—
2.72 N NaOH + M/1 R.S.	103	194	91	0.53
6.97 N NaOH	106	—	—	—
6.97 N NaOH + M/1 R.S.	52	120	68	0.435
13.9 N NaOH	36.2	—	—	—
13.9 N NaOH + M/1 R.S.	1.19	43.25	42.06	0.0275
N/1 KCl	121	—	—	—
N/1 NaCl	91	—	—	—
N/1 NaCl + N/1 KCl	188	212	24	0.89

Phase Rule Study

Determinations of the solubility of Rochelle salt in increasing concentrations of caustic soda were carried out in a thermostat at 25°. The wet solid phase was also analyzed and the results plotted by Schreinemaker's method. It is of course realised that, by the definition of a component, it must not undergo decomposition, whilst it is probable that in complex formation the Rochelle salt does decompose. Nevertheless, it was thought that the form of the curves would throw light on the matter, as indeed they do. The results are contained in Table IV.

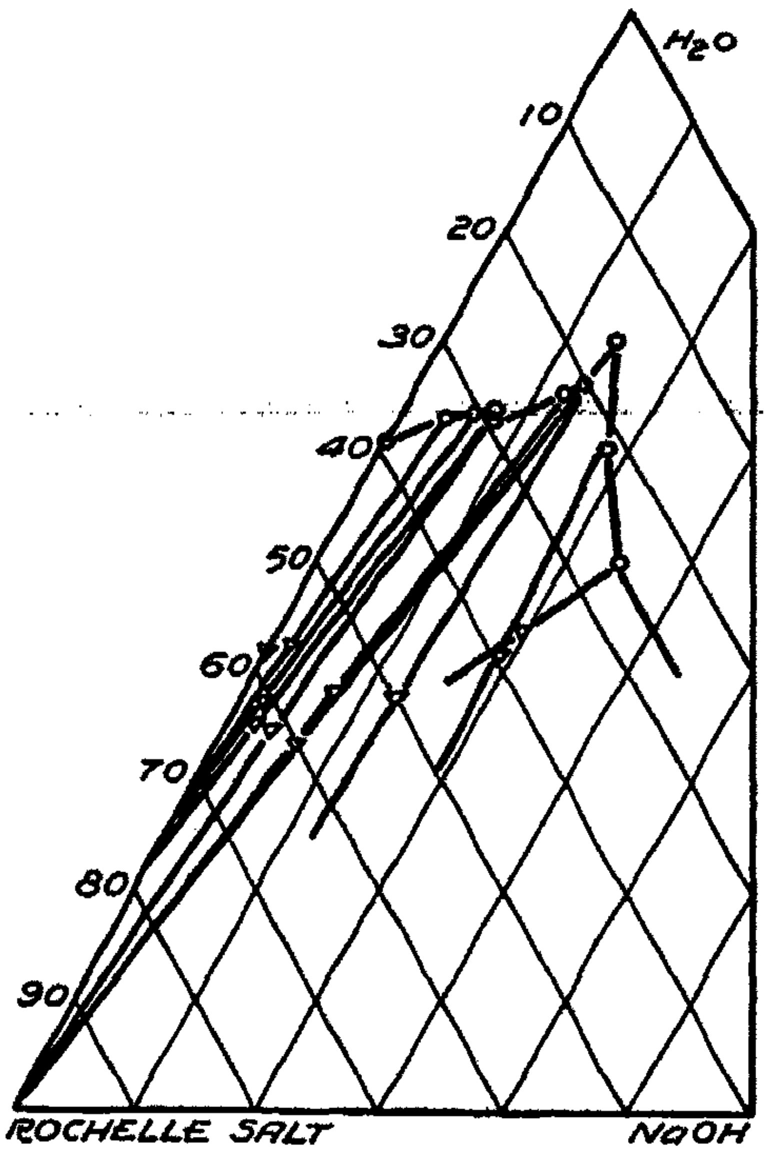

FIG. 1

Rochelle Salt, Caustic Soda and Water. Temp. 25°C.

TABLE IV

Exp. No.	Liquid Phase			Wet Solid Phase		
	R.S.	NaOH	H_2O	R.S.	NaOH	H_2O
1.	39%	—	61%	58%	—	42%
2.	33.3	3.7	63.0	56.0	1.68	42.33
3.	31.0	5.8	63.2	61.3	2.0	36.7
4.	29.0	7.25	63.75	62.5	2.6	34.9
5.	29.5	7.6	62.9	61.7	3.9	34.4
6.	20.2	13.5	66.3	60.3	6.1	33.6
7.	22.6	12.2	65.2	54.7	7.8	37.5
8.	16.1	13.85	70.05	50.0	12.5	37.5
9.	21.6	15.3	63.1	39.6	19.0	41.4
10.	25.7	23.9	50.4	36.9	19.4	43.7

Beyond the NaOH concentration of experiment 10 it was found impossible to proceed owing to the great viscosity of the solution. When the above figures are plotted on triangular paper, it becomes obvious that about 7% NaOH the solid phase becomes anhydrous Rochelle salt. About 13% NaOH a further point of inflection occurs. That the solid phase here is NaOH seems very improbable, judging by the direction of the tie-lines. In view of what was said at the beginning of this section, it is not to be expected that the tie-lines should intersect in this latter region. It is worthy of note that the points of inflection are accompanied by marked changes in the appearance of the solid phase. At the second point of inflection, the solid phase assumes a structure resembling a gel, whilst the liquid phase might be compared to a synerised liquid. As the concentration of NaOH is increased the bulk of the "gel" increases until eventually the liquid portion disappears or, at all events, becomes unfilterable by suction.

Conclusion

The specific rotations of Rochelle salt in various concentrations of alkali, and for different regions of the spectrum have been determined. The very marked variation is accounted for on the hypothesis of complex formation. This hypothesis receives considerable support from the experimental evidence presented. This rests upon:

1. Reduced OH′ concentration in solutions of NaOH containing Rochelle salt.

2. Much reduced conductivity on mixing solutions of Rochelle salt and NaOH.

3. The form of the phase rule diagram.

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THERMODYNAMICS OF LEAD BROMIDE[1]

BY JESSIE Y. CANN AND RUTH A. SUMNER

The purpose of this investigation is to determine, by means of electromotive force measurements, the free energy of formation, ΔF, the change of entropy, ΔS, the change in heat content, ΔH, and the activity coefficient, γ, of lead bromide.

Free Energy of Lead Bromide

The published measurements of the potential of the cell corresponding to the reaction

$$Pb_{(s)} + 2\ AgBr_{(s)} = PbBr_{2(s)} + 2\ Ag_{(s)}$$

are not concordant. We therefore have measured the cell Pb (in Sat. Amalg.), $PbBr_{2(s)}$, $PbBr_{2(sat.)} + KBr_{(aq)}$, $AgBr_{(s)}$, $Ag_{(s)}$ in which the electrolyte was a *saturated solution* of lead bromide in 0.01, 0.025, and 0.1 M KBr to which a small amount of hydrobromic acid had been added.

The lead bromide used by J. Y. Cann was a portion of the same material which was used by Randall and Vietti,[2] and which had been re-crystallized four times from conductivity water.

The potassium bromide solution was prepared from high-grade "analyzed" material, and the hydrobromic acid was a dilute solution of a pure acid through which hydrogen had been bubbled to remove traces of bromine. The lead amalgam was of the same supply as that used for the determination of the potential of the lead electrode.[3]

The silver bromide spirals were prepared by electrolyzing silver oxide—silver spirals prepared as previously described,[3] in a 0.1M solution of potassium bromide. The lead amalgam and spirals were freed from absorbed film or gases, and the solutions introduced as described previously.[3]

The cells were the ordinary H-cells of Pyrex, and the thermostat was either the ordinary oil thermostat regulated for 25°, or the one used by Gerke, fitted with an easily adjustable thermo-regulator. The thermometer was a mercury thermometer which was checked against a standard resistance thermometer that had been calibrated by the U. S. Bureau of Standards.

Nine cells were made up. Cells 1, 2, 3, and 4 contained 0.01 M KBr. The first cell, which had lead bromide only over the lead amalgam, gave un-

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[1] This problem was suggested by Merle Randall, and the experimental part of the work was started at the University of California by J. Y. Cann on sabbatical leave from Smith College, and continued by R. A. Sumner at Smith College as partial fulfillment of the requirements for Special Honors in Chemistry. Charlotte Klingler, Graduate Student at Smith College, has repeated the results of the authors, having made four cells, each of which gave a steady constant value of $E^\circ_{298\cdot1} = 0.3465$, agreeing precisely with the results obtained previously.

[2] Randall and Vietti: J. Am. Chem. Soc., 50, 1526 (1928).

[3] Randall and Cann: J. Am. Chem. Soc., 52, 589 (1930).

TABLE I

The cell Pb (in sat. amalg.), Pb $Br_{2(s)}$, Pb Br_2 (sat.) + $KBr_{(aq)}$, Ag $Br_{(s)}$, $Ag_{(s)}$

T	Cell 3	T	Cell 5	T	Cell 7	T	Cell 8	T	Cell 9
25	0.34693	25.86	0.34639	25.66	0.34702	28.55	0.34540	25	0.34840
25	0.34691	30.44	0.34500	30.14	0.34532	27.75	0.34567	25	0.34822
		35.02	0.34360	35.52	0.34357	25.46	0.34627	25	0.34811
		40.11	0.34214	40.41	0.34234	20.85	0.34855		
		28.20	0.34546	28.35	0.34578	19.37	0.34894		
25	0.34 690	18.03	0.34849	23.36	0.34740	17.87	0.34922	25	0.34810
						47.80	0.33987		

TABLE II

The cell Pb (sat. amalg.), $PbBr_{2(s)}$, $PbBr_2$ (sat.) + $KBr_{(aq)}$, $AgBr_{(s)}$, $Ag_{(s)}$

T	Cell 1	T	Cell 2	T	Cell 3	T	Cell 4	T	Cell 6	T	Cell 8
19.30	0.34912	21.04	0.34982	19.25	0.34996	19.4	0.34838	19.72	0.34934	21.00	0.35088
23.40	0.34750	22.75	0.35884	23.40	0.34858	22.75	0.35858	21.05	0.34893	22.75	0.34931
25.30	0.34684	25.00	0.34864	25.30	0.34798	25.00	0.34822	22.75	0.34827	25.10	0.34858
26.20	0.34626	26.12	0.34808	26.14	0.34839	26.15	0.34789	26.25	0.34744	26.20	0.34840
32.00	0.34440	31.98	0.34604	31.95	0.34624	31.98	0.34615	32.05	0.34569	31.95	0.34558
35.00	0.34349	35.25	0.34503	35.00	0.34484	34.95	0.34524	35.25	0.34485	35.08	0.34405

satisfactory results and was discarded. No. 2, a large cell, gave $E_{298.1} = 0.3531$ V which gradually decreased to 0.3519 V. This contained only 0.5 cm. layer of solid lead bromide in each side of the H-cell. No. 3, a very small cell, with a larger quantity of solid lead bromide, gave 0.3482 V at 25° after about seven days; but after standing in the thermostat for over thirty days the potential became constant at $E_{298.1} = 0.3469$ V which agrees with the potential of three other cells. No. 4, the same type of cell as No. 2, gave a very constant potential of 0.3498 V during about two weeks; but we feel, in view of later developments, that the amount of solid lead bromide (1 cm layer) was not sufficient. Cell No. 5 contained 0.1 M potassium bromide and enough solid lead bromide to completely cover the silver-silver bromide spiral. The cell was taken through the temperature range from 15° to 42° and back again four times, and about seventy-five values, taken after the initial erratic period of three days, during which time the value of the potential rapidly decreased at the constant, initial temperature of 25°, were plotted, a few of which (taken at random) are shown in Table I. Cell No. 6 contained 0.025 M potassium bromide, was erratic and discarded. Cells No. 7 and 8 contained 0.025 M potassium bromide with enough solid lead bromide to fill the cell to the middle of the cross of the H. No. 7 was taken through the temperature cycle twice and agreed with Cell No. 5. Cell No. 8 was high at the beginning, but after the traverse of a temperature cycle of fourteen days, agreed with the previous cells. Cell No. 9 contained 0.1 M potassium bromide with a very large amount of solid lead bromide and gave results in agreement with Cells 3, 5, 7 and 8. Random potentials of these cells are given in Table I.

Nine cells were prepared by R. A. Sumner.

Numbers 1 and 2 contained 0.1 M KBr,
3 and 4 contained 0.01 M KBr,
5 and 6 contained 0.05 M KBr, and
7 and 8 contained 0.025 M KBr.

These cells were made up in exactly the same manner as the last and best ones prepared by J. Y. Cann. Numbers 5 and 7 gave erratic values and were discarded. Numerous readings, over a period of a year, were taken on cells 1, 2, 3, 4, 6 and 8, and Table II gives a list of representative values at various temperatures.

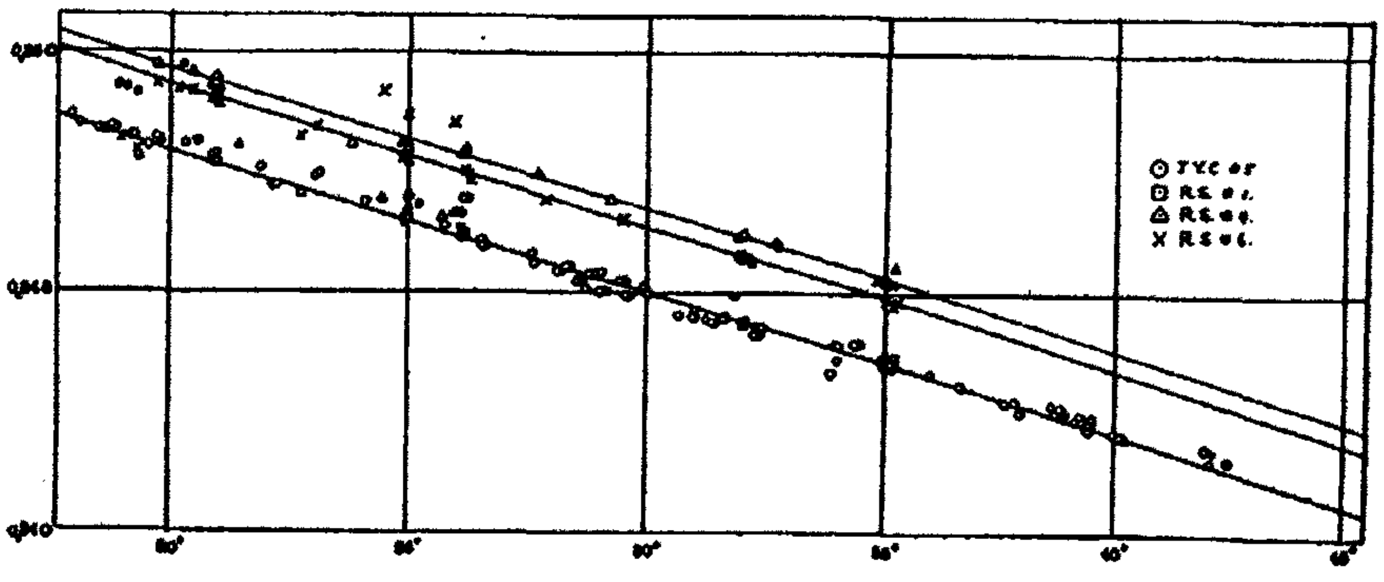

FIG. 1

In addition, four cells were prepared by C. Klingler. These all contained 0.1 M KBr. These last cells came to equilibrium within a day or two and gave steady, constant values of $E^\circ_{298.1} = 0.3465$ at 25°C. This checking of results by three independent workers convinces us that our method of preparing the cells and the values obtained, are correct.

Curve I shows the measured potentials of the best cells.

All the measured potentials were plotted against the temperature and from the best average curve we find

$E_{298.1} = 0.3465\text{V}; dE/dt_{(298.1)} = -0.000289$ V/o.

Whence

$$\text{Pb (in sat. amalg.)} + 2\,\text{AgBr}_{(s)} = \text{PbBr}_{2(s)} + 2\,\text{Ag}_{(s)};$$
$$\Delta F_{298.1} = -15995 \text{ cal.}, \Delta S_{298.1} = -13.34 \text{ Cal./o}; \quad \Delta H_{298.1} = -19972 \text{ cal.} \qquad (1)$$

Combining with the data of Gerke[4] for the formation of saturated lead amalgam, we find

$$\text{Pb}_{(s)} + 2\,\text{AgBr}_{(s)} = \text{PbBr}_{2(s)} + 2\,\text{Ag}_{(s)}; \Delta F^\circ_{289.1} = -16258 \text{ cal};$$
$$\Delta S^\circ_{298.1} = -12.599 \text{ cal./o}; \Delta H^\circ_{298.1} = -20014 \text{ cal.} \qquad (2)$$

Then combining with Randall and Halford's[5] value for

$$2\,\text{Ag}^\circ + \text{Br}_2^\circ = 2\,\text{AgBr}; \Delta F^\circ_{298.1} = 2\,(-22917) \text{ we find} \qquad (3)$$

$$\text{Pb}^\circ + \text{Br}_2^\circ = \text{PbBr}_2; \Delta F^\circ_{298.1} = -62092 \text{ cal.} \qquad (4)$$

This value is in good agreement with the value of Latimer[6] i.e. $\Delta F^\circ_{289.1} = -62{,}065$ Cal. It also agrees with that of Krahmer[7] i.e. $\Delta F^\circ_{298.1} = -62057$ cal.

Combining our value $\Delta S_{298.1} = -12.599$ for $\text{Pb}_{(s)} + 2\,\text{AgBr}_{(s)} = \text{PbBr}_2(s) + 2\,\text{Ag}(s)$ with $\Delta S^\circ_{298.1} = -0.96$ for AgBr obtained from the reaction $S_{\text{Ag}^\circ} + S_{\text{Br}^\circ} \rightarrow S_{\text{AgBr}^\circ}$, using the values $S_{\text{Ag}^\circ} = 10.25$, $S_{\text{Br}^\circ} = 16.3$ and $S_{\text{AgBr}} = 25.59$[8] we find for the reaction, Elements

$$\text{PbBr}_2; S^\circ_{298.1} = -14.519, \qquad (5)$$

whereas Latimer[6] obtains −12.63; thus showing a difference of 1.889 entropy units. It was because of this difference, dependent upon the temperature coefficient of the cell, dE/dT, that the experimental work has been checked by three individuals.

Combining $\Delta H^\circ_{298.1} = -20014$ for the reaction $\text{Pb} + 2\,\text{AgBr} = \text{PbBr}_2 + 2\,\text{Ag}$ with Bichowsky's[9] value of $\Delta H^\circ_{298.1} = -23840$ for AgBr, we obtain $\Delta H^\circ_{298.1} = -67694$ for $\text{Pb} + \text{Br}_2 = \text{PbBr}_2$ (6)

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[4] Gerke: J. Am. Chem. Soc., **44**, 1684 (1922).

[5] Randall and Halford: J. Am. Chem. Soc., **52**, 192 (1930).

[6] Latimer and Hoenshel: J. Am. Chem. Soc., **48**, 19 (1926).

[7] Krahmer: Z. Elektrochemie, **26**, 97 (1920).

[8] The value 25.59 is an average of 25.62, obtained by Eastman and Milner (personal communication) and 25.56 obtained by Eucken, Clusius and Woitinek: Z. anorg. Chem., **203**, 39 (1931).

[9] Intern. Crit. Tables, Vol. V.

For this value Gerke[10] obtained −67480.

Using the third law and our values of $\Delta F^\circ_{298.1} = -62092$ and of $\Delta S^\circ_{298.1} = -14.519$, we find $\Delta H^\circ_{298.1} = -66420$. Braune and Koref[11] found $\Delta H^\circ_{298.1} = -66350$. If now we use Latimer's[6] value of $\Delta S^\circ_{298.1} = -12.63$ for $PbBr_2$, and employ the third law, we find $\Delta H^\circ_{298.1} = -65857$. Krahmer[7] found $\Delta H^\circ_{298.1} = -65580$ and Thomsen[12] found −64456. We take the value of $\Delta H^\circ_{298.1} = -67694$ as correct.

Activity Coefficient of Lead Bromide

Randall and Vietti[2] have determined the solubility of $PbBr_2$ in KBr solutions. They state that by graphical methods they have been unable to determine the activity coefficient of $PbBr_2$ in KBr consistent with other data. Using their data and plotting log $1/m\pm$ against $\mu^{\frac{1}{2}}$, and extrapolating to zero concentration, we found the proportionality factor 46.82. Then by dividing any value of $1/m\pm$ by this value,[13] we found the corresponding value of the activity coefficient, $\gamma\pm$. Table III gives a tabulation of these values.

TABLE III

M KBr	M $PbBr_2$	$m\pm$	log $1/m\pm$	$1/m\pm$	$\mu^{\frac{1}{2}}$	$\gamma\pm$
0.001	0.02645	0.0425	1.3715	23.5215	0.2835	0.5024
0.002	0.02611	0.0425	1.3716	23.5302	0.2834	0.5025
0.005	0.02500	0.0423	1.3738	23.6471	0.2828	0.5050
0.01	0.02345	0.0423	1.3732	23.6162	0.2835	0.5044
0.02	0.02043	0.0423	1.3737	23.6423	0.2851	0.5049
0.025*	0.01845*	0.0413	1.3835	24.1847	0.2835	0.5165
0.05	0.01380	0.0436	1.3601	22.9157	0.3023	0.4894
0.1	0.00859	0.0490	1.3094	20.3008	0.3546	0.4355
0.2	0.00694	0.0682	1.1661	14.6589	0.4684	0.3131
0.374	0.00687	0.1011	0.9953	9.9893	0.6282	0.2113

* Interpolated value.

In order to determine the activity coefficient from *electromotive force* measurements, use is made of the following equation: $E = -3RT/2F \ln (k^1\gamma \pm m \pm)$, in which[14] the constant k^1, which includes E°, may be found by substituting a value of $\gamma\pm$, found by some other method, together with the appropriate values for the related quantities, and solving for k^1. For this purpose we chose Randall and Vietti's value of $\gamma\pm$ in 0.01 m KBr soln, and found the value of k^1 to be 0.0058411. Using this value, $\gamma\pm$ for the other concentrations of KBr was calculated. The values thus obtained for the concentrations 0.025, 0.05 and 0.1 m are as follows:

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[10] Gerke: Chem. Reviews, **1**, No. 4, 377 (1925).

[11] Braune and Koref: Z. anorg. Chem., **87**, 175 (1914).

[12] Thomsen: Landolt-Börnstein Tabellen, **2**, 1533 (1923); J. prakt. Chem., (2), **12**, 92 (1875).

[13] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," 371 (1923); J. Am. Chem. Soc., **43**, 1112 (1921).

[14] Ref. 12, p. 355.

m KBr	$\gamma\pm$ E.M.F.	$\gamma\pm$ Sol'y.
0.025	0.51661	0.5165
0.05	0.48936	0.4894
0.1	0.43543	0.4355

The solubility data are listed for purposes of comparison. It will be seen that these values of $\gamma\pm$ from electromotive force measurements are practically identical with those obtained from solubility measurements. Too much weight, possibly, should not be laid upon this identity because the method of calculation was relative, not absolute. Nevertheless the agreement is remarkable.

We also calculated the product, $K_{S.P.} = 4m\pm^3 \gamma\pm^3$, for $PbBr_2$, and found it to be 0.0000389.

Recent papers by Fromherz[15] discuss the activity coefficients of the lead halides in great detail. He states repeatedly that the true activity coefficients of an electrolyte like $PbBr_2$ agree closely with those of the strong electrolyte $BaCl_2$. Our results are in general accordance with this statement.

Summary

We have calculated the values of ΔF, ΔH and ΔS for the formation of lead bromide from its elements. Our values of ΔF and ΔH agree reasonably well with those found in the literature. Our value of ΔS differs from Latimer's value because the coefficient dE/dT would seem to be too large.

We have also calculated the values of the activity coefficient from both electromotive force measurements, using our own data, and from solubility measurements, using the data of Randall and Vietti. A relative method of calculation was used.

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Northampton, Massachusetts.

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[15] Fromherz: Z. physik. Chem., **153**, 376; 321 (1931).

THE POLYIODIDES OF RUBIDIUM

I. Iodine and Rubidium Iodide

BY T. R. BRIGGS AND E. S. PATTERSON

Temperature-composition data for the system iodine and potassium iodide and for the system iodine and cesium iodide, at a pressure of approximately one atmosphere, have been reported in earlier papers[1] in this series. In the first of these systems, no solid compound (such as KI_3) was found in equilibrium with the melt, whilst in the second system the compounds (polyiodides) CsI_3 and CsI_4 were definitely shown to be produced.[2] The present communication presents the data for the system iodine and rubidium iodide, which system, as it will appear in the sequel, turns out to be intermediate as regards the other two.

The experimental technique employed in this investigation was the same as that described in the earlier papers and needs no further comment. The data required for the construction of the phase diagram were obtained from temperature arrests in the cooling curves, from the boiling points of mixtures of known composition and from analyses of saturated liquid phases (melts). The method used in the analysis will be found in the earlier papers.

The iodine was purified by being sublimed and it was dried carefully before it was used. The rubidium iodide (from Kahlbaum) was recrystallized once from water and then dried. The combined iodine in the product was then determined by analysis and it was found to be 97.8 per cent of that required by the formula RbI. The salt was thus considered to be sufficiently pure for the purpose of the investigation.

The various types of data which were obtained are presented in Tables I, II and III.

The temperature-composition diagram is shown in Fig. 1. The solid triiodide RbI_3 certainly exists below 188°, but there is no indication of a higher polyiodide such as RbI_4, analogous with CsI_4. The triiodide melts incongruently at about 188°, decomposing into RbI and iodine above this temperature. The solubility of RbI in iodine, like that of KI and of CsI, is almost independent of the temperature; and because of this, no temperature arrest due to the separation of solid RbI was discernible in the cooling curve for Mixture 12 in Table I. The (constant) boiling point of melts saturated with RbI lies at about 238° and a special determination of the eutectic point made it possible to place the latter at 80.8° and 17.4 mole per cent RbI.

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[1] Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930); Briggs: 34, 2260 (1930).

[2] Cf. also the ternary system iodine, cesium iodide and water. Briggs, Greenawald and Leonard: J. Phys. Chem., 34, 1951 (1930).

TABLE I

Temperature Arrests (°C)

Mixture Number	Mole Per Cent RbI	1st Arrest	2nd Arrest
1	0	114	none
2	5	108.8	80.6
3	10	100.0	80.8
4	15	87.0	80.8
5	17	81.8	80.8
6	20	103	80.7
7	25	134	81.0
8	30	149	81.0
9	35	167	80.0
10	40	178	81.0
11	42.5	185	81.5
12	45	187.2	79.0
13	47.5	187.8	79.0
14	50	188	none
15	52.5	187.5	none
16	55	187.5	none
17	60	189	none
18	65	188	none
19	70	190	none
20	85	189	none

TABLE II

Composition of the Saturated Liquid

A. Original Mixture containing 42 Mole Per Cent RbI

Temperature	Mole Per Cent RbI
81 (eutectic)	17.44
142	26.35
160	32.16
175	37.60

B. Original Mixture containing 55 Mole Per Cent RbI

Temperature	Mole Per Cent RbI
195	44.71
206	45.23
220	45.62
238.5 (B. P.)	46.23

TABLE III

Boiling Points (°C)

Mixture Number	Mole Per Cent RbI	Boiling Point	Mixture Number	Mole Per Cent RbI	Boiling Point
1b	0	184	6b	50	*236
2b	10	187	7b	60	*238.5
3b	20	195	8b	70	*238.5
4b	30	207	9b	80	*238
5b	40	225	10b	90	*239

*Constant, others rising with time.

Wells, Wheeler and Penfield,[1] in their celebrated investigation of the polyiodides, reported the existence of RbI_3 as solid phase in aqueous systems of iodine and rubidium iodide. They were unable to prepare a higher polyiodide of rubidium, such as RbI_5, analogous with the higher polyiodide of cesium, to which they had assigned the formula CsI_5.[2] They stated that the triiodide "melts" at 194° in an open tube and at 190° in a closed tube, and that it "whitens" at 270° because of the loss of the polyhalide iodine. The "melting" point of Wells and his coworkers is evidently the transition point (188°) for the system RbI_3, RbI and melt. Their temperature of whitening, however, is unnecessarily high, for the melt saturated with RbI boils at 238° and the vapor must consist virtually of pure iodine. The present investigation thus confirms in all essential respects, the findings of Wells, Wheeler and Penfield. It also confirms the work of Foote and Chalker,[3] who showed that a single polyiodide, presumably RbI_3, exists as solid phase in the ternary system iodine, rubidium iodide and water at 25°.

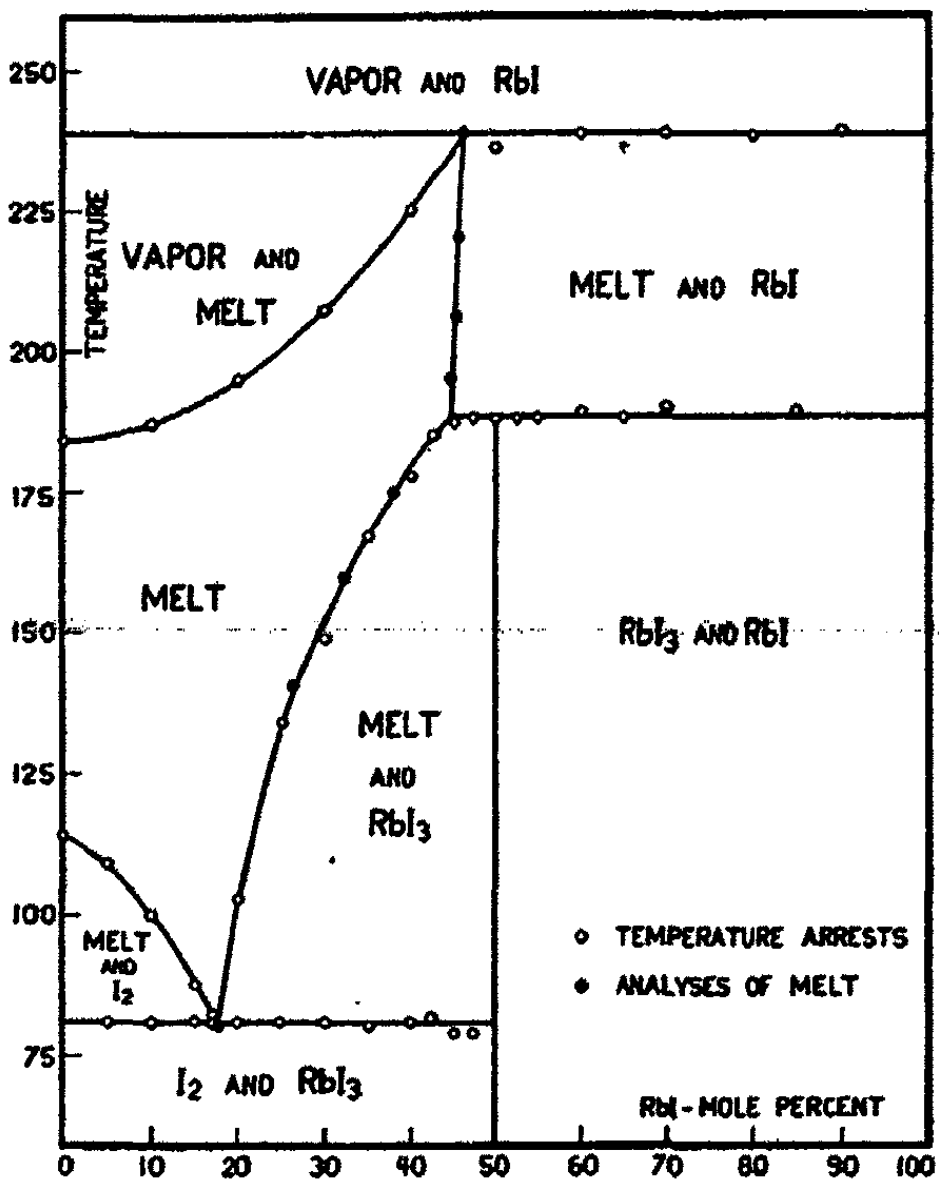

Fig. 1

The System I_2—RbI at approximately 1 atm.

Abegg and Hamburger,[4] in their work on the ternary system containing benzene, reported the higher polyiodides RbI_7 and RbI_9 in addition to the

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[1] Am. J. Sci., (3), 43, 475; 44, 43 (1892).

[2] Cf. Briggs, Greenawald and Leonard: J. Phys. Chem., 34, 1951 (1930); Briggs: 34, 2260 (1930).

[3] Am. Chem. J., 39, 561 (1908).

[4] Z. anorg. Chem., 50, 403 (1906).

triiodide RbI_3. There is no indication of these higher polyiodides in the binary system, and if they do exist in the ternary system, it seems reasonable to suppose that they must be ternary compounds containing benzene.[1]

In that part of their paper which deals with the binary system iodine and potassium iodide, Abegg and Hamburger stated that a mixture of iodine and rubidium iodide, corresponding in composition to the supposed compound RbI_9, melted at 81.3°. It is now apparent that this is the eutectic temperature and not the melting point of a compound; Abegg and Hamburger were not dealing with RbI_9, as they supposed, but with a mixture of iodine and RbI_3. They made the same mistake here that they made in the system iodine and potassium iodide—that is to say, they took the eutectic temperature to be the melting point of a polyiodide. The probable explanation of this curious error and the consequences which it produced have been discussed at length in the paper by Briggs and Geigle.

In connection with the work reported in this paper, various other systems containing a halogen and an alkali-metal halide have been investigated. These systems were: iodine and sodium iodide, iodine and sodium chloride, iodine and sodium bromide, iodine and potassium chloride, iodine and potassium bromide, bromine and potassium bromide. The temperature arrests and the boiling points of mixtures of known composition showed that in every case the components are immiscible. The same is true of calcium iodide and iodine as a binary system, but it is interesting to find that investigation of the ternary system iodine, calcium iodide and water, now under way in this laboratory, shows that iodine is extremely soluble in mixtures of calcium iodide and water, and that at least one *hydrated* calcium polyiodide is present as solid phase in the ternary system at 25°. We thus find no polyiodide of calcium in the binary system and not even any dissolving of calcium iodide by liquid iodine, yet the miscibility is extraordinarily great in the ternary system containing water and there is evidence of a polyiodide when water is the third component. This is strong confirmation of the position taken by Grace and accepted by Foote and Bradley.

Summary

The results of this investigation may be summarized as follows:

1. The temperature-composition diagram for the system iodine and rubidium iodide has been determined from 60° up to the boiling point of the saturated melt (238°).

2. The solid phases in contact with melt are iodine, rubidium triiodide (RbI_3) and rubidium iodide. The triiodide melts incongruently at 188°. No indication of a higher polyiodide, analogous for example with cesium tetraiodide, was obtained.

3. Iodine and rubidium iodide, as one would expect, is thus intermediate between iodine and potassium iodide (solid phases iodine and KI) and iodine and cesium iodide (solid phases iodine, CsI_4, CsI_3 and CsI).

Cornell University,
June, 1932.

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[1] Cf. Grace: J. Chem. Soc., **1931**, 594; Foote and Bradley: J. Phys. Chem., **36**, 683 (1932).

OSMOTIC PRESSURE AND THE PERMEABILITY OF MEMBRANES

BY W. W. LEPESCHKIN*

Introduction

The author's experiments twenty years ago showed that the variation movements of plants are caused by a change of the turgor pressure in the pulvinus cells produced by the variation of the permeability of protoplasm to substances dissolved in the cell sap. Turgor pressure is a hydrostatic pressure caused by osmotic pressure. Thus the problem of the influence of the permeability of protoplasm upon turgor pressure is really a problem of the influence of the permeability of a membrane upon the hydrostatic pressure in the osmometer. This problem interested not only physiologists but also chemists, since no other explanation than the permeability of the membrane could be given for the discrepancy between the osmotic pressure calculated according to the van't Hoff-Arrhenius formula and that observed in an osmometer. If it was not this explanation, one had to admit with Kahlenberg[1] that osmotic pressure and gas laws are different, and although the new porous disc method of measuring osmotic pressure seems to be able to annihilate all doubt concerning the similarity of these laws, the problem of the cause of a too low pressure in the osmometer can scarcely be considered as solved.[2]

One explains a too low pressure in the osmometer mostly by the supposition that due to the penetration of the solute through the membrane the solvent under the membrane is gradually transformed into a more and more concentrated solution, the osmotic pressure of which brings that of the solution in the osmometer into a partial equilibrium. This supposition lies in the basis of Tammann's considerations of the dependence of the pressure observed in an osmometer upon the permeability of membranes to solutes.[3] Tammann came to the conclusion that the ratio $P-P_b/2P$ where P is the theoretical osmotic pressure calculated according to Arrhenius and van't Hoff and P_b is the pressure observed in the osmometer, is approximately constant and proportional to the permeability of the membrane to the solute.

A quite different principle lies in the basis of v. Antropoff's calculation of the dependence of the pressure in an osmometer upon the permeability of the membrane.[4] Supposing that the solution formed under the membrane is continuously replaced by the solvent, v. Antropoff came to the conclusion that the pressure in an osmometer should depend not only upon the permeability of the membrane to the solute but also upon that to the solvent. Indeed,

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[1] Kahlenberg: Trans. Wisconsin Acad. Sci., **15**, 209 (1906).

[2] R. V. Townend: J. Am. Chem. Soc.. **50**, 2958 (1928); F. T. Martin and L. H. Schultz: J. Phys. Chem., **35**, 638 (1931).

[3] G. Tammann: Z. physik. Chem., **9**, 97 (1892).

[4] A. von Antropoff: Z. physik. Chem., **76**, 721 (1911).

the pressure in an osmometer is actually produced by the penetration of the solvent through the membrane into the osmometer and results in consequence of an increase of the volume of the liquid in the osmometer. But this volume depends not only upon the volume of the solvent coming into the osmometer but also upon the volume of the solute going out of the osmometer through the membrane. The maximum pressure in the osmometer is evidently reached when both volumes become equal. V. Antropoff gives the following formula which expresses the dependence of the maximum pressure in the osmometer P_m upon the permeability of the membrane to solvent σ' and that to solute σ: $P_m = P(1 - \sigma/\sigma')$ where P is the theoretical osmotic pressure. The testing of this formula was made by v. Antropoff on the basis of Cohen and Commelin's experimental data concerning the osmotic pressure of sugar-pyridin solutions. Comparing the calculated and experimental values of the pressure in the osmometer given in v. Antropoff's paper we may come, however, to the conclusion that the former are always greater than the latter, and sometimes the calculated pressure is more than twice as great as the observed one. V. Antropoff promised to give later his own experimental data concerning the same problem, but these data were not published during the next twenty years. The present experiments have as a purpose the explanation of the discrepancies just mentioned and show that Tammann's results as well as those of v. Antropoff should be considered in finding a mathematic scheme of the dependence of the hydrostatic pressure in the osmometer upon the permeability of the membrane.

Osmometer and Determination of the Maximum Hydrostatic Pressure

The maximum hydrostatic pressure in the osmometer was determined in the present experiments by the method similar to that used by Berkeley and Hartley,[5] that is by finding a pressure in the osmometer which just prevents the sucking of water into the osmometer. The membrane used was parchment paper obtained from the Thomas Co., Philadelphia. Preliminary experiments showed that this membrane could be used for several months without any visible change of its chemical properties, being not affected by water or bacteria. This parchment paper had an average thickness of 0.180 mm. and soaked with water was thicker by twenty percent. The membrane was attached to an osmometer (o, Fig. 1) made of glass and fastened to a brass ring r to which the membrane m was stuck with a mixture of black sealing wax and venetian turpentine. The edges of the membrane were covered with a brass ring R attached to it by means of the same mixture. Both rings were pressed together by six brass clamps c which were gradually screwed on while the rings were heated and sealing wax melted. In order to fill all small cavities inside of parchment paper with water the osmometer was immersed in boiled and cooled water for some days (water surface covered with oil). The osmometer filled with a solution was then closed with a rubber stopper through which a thermometer t (divisions 0.1°C) and a glass tube a were inserted, and placed in water of a thermostat bath (Freas', capacity 50 liters). Water was

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[5] Earl of Berkeley and E. G. J. Hartley: Phil. Trans., **206A**, 481 (1906); **209**, 177 (1909).

continuously stirred in the latter. The temperature in the osmometer was always adjusted to 25°C ± 0.02°C. Water used for the bath as well for the solutions in the osmometer was spring water (laboratory tap water). It contained 0.029 percent dissolved substances (CaO 0.004%, MgO 0.002%, K_2O and Na_2O 0.003%, Cl 0.092%, SO_3 0.004%, SiO_2 0.003%, CO_2 0.008%) and had pH = 7.3.

The tube a (Fig. 1) was connected (thick wall rubber tube) with the other part of the instrument in which the volume of water filtered through the membrane or sucked into the osmometer was measured. This part consisted of an exactly horizontal capillary tube b provided with a three channel glass cock d, the upper branch of which was connected with a funnel and served for filling the instrument with water or with the same solution with which the osmometer was filled. Air bubbles were carefully driven out. The lower branch of the cock was united with the osmometer by a thick wall rubber tube. The capillary tube had a short branch e provided with a rubber ball which could be squeezed by means of a clamp and served for filling the capillary tube with the liquid when it was disconnected from the funnel but connected with the osmometer. In this case the filtration of water through the membrane produced a movement of the meniscus in the capillary tube to the right, the sucking in of water its movement to the left. Every movement of the meniscus in the capillary tube by one division of the millimeter scale corresponded to 0.002015 cc of water passing through the membrane. The height of the capillary tube above the water level in the thermostat bath represented the pressure expressed in cm of the column of water or the solution used. In tables below the pressure is expressed in cm of water column. When the pressure used was greater than 200 cm it was produced by mercury. For this purpose a U-shape tube was inserted between the osmometer and the capillary tube, and the latter as well as a half of the U-shape tube was filled with mercury.

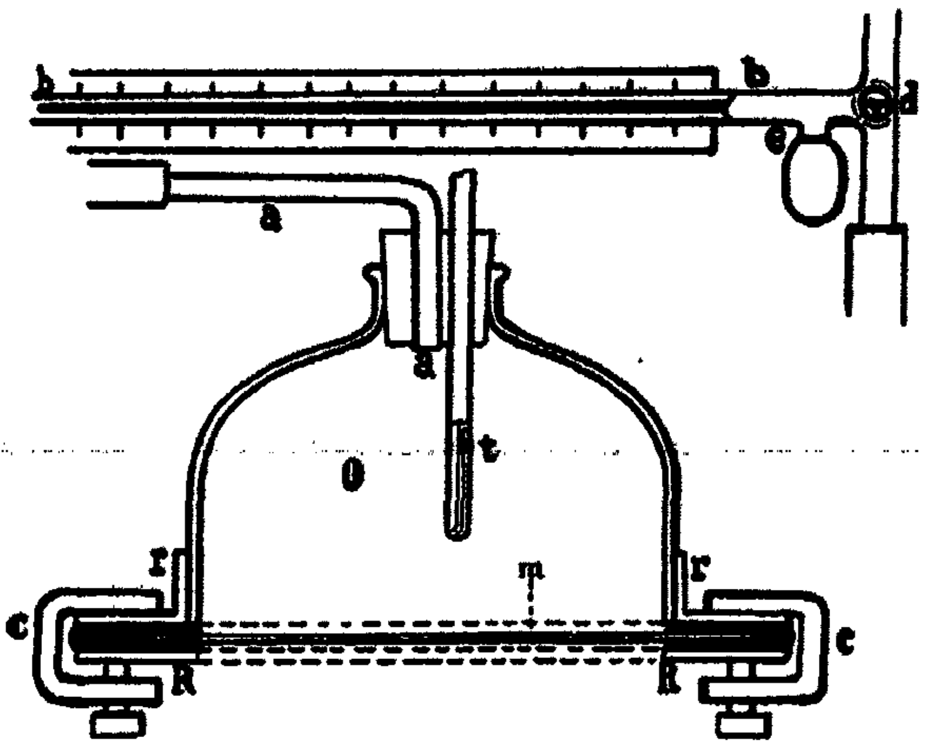

FIG. 1

Osmometer. Explanation is given in the text. The black line on the scale is thicker at the right than at the left.

The same osmometer was used for the filtration of water and solutions to determine the permeability of the membrane to water, and for the determination of the osmosis rate of the solute through the membrane (permeability to solute). The diameter of the lower opening of the osmometer covered by the membrane, and therefore that of the part of the membrane through which the filtration or osmosis took place was 7.4 cm. The area of this part after the osmometer was filled with water or solutions and the membrane stretched was about 55.6 sq. cm. The volume of the osmometer was 289 cc. Every change of temperature in the osmometer by 0.1°C produced therefore a movement of the meniscus in the capillary tube by 3.7 divisions. This was considered in all experiments. In a few experiments (indicated below) the osmometer was immersed in a cement trough of a sink (cubic form, capacity 45 liters), filled with water. In this case the temperature varied more, and the correction was necessary.

Preliminary experiments showed that by the stretching of the membrane an increase of the pressure in the osometer was completed in two to three hours when this increase was greater than 100 cm of water column. A smaller change of the pressure correspondingly required less time for the settlement of the equilibrium. About two hours were necessary for the temperature equilibrium. Accordingly, the observation of the meniscus always began three hours after the immersion of the osmometer in the thermostat bath and its connection with the capillary tube. The pressure was changed several times until a pressure was found which did not produce any filtration or sucking in of water through the membrane during a certain period of time (one to four hours). This pressure was considered as equal to the maximum pressure which can be reached in the osmometer. The concentration of the solution in the latter was determined immediately after the determination of this pressure.

Sodium chloride (Merck, blue label) was used in these experiments as solute. Its concentration was determined by titration with silver nitrate (potassium chromate as indicator). From the amount of chlorine found in the solution its amount contained in water was substracted.

Is the Accumulation of Solute under the Osmometer responsible for a too Low Pressure?

It is well known that the maximum hydrostatic pressure in the osmometer with parchment paper as a membrane is many times smaller than the osmotic pressure calculated according to the van't Hoff-Arrhenius formula. Is the accumulation of solute in water under the osmometer responsible for this low pressure? Even if the solute passing through the membrane should form a solution under the membrane which falls down at the bottom of the vessel, one could think that a layer of the solution always remains under the lower surface of the membrane balancing by its osmotic pressure the most part of the osmotic pressure in the osmometer. It is very easy to prove, however, that a continuous stirring of the liquid under the osmometer does not increase the hydrostatic pressure in the osmometer. The following experiments prove that even the removal of the very thin layer of the solution from the lower surface of the membrane does not increase the maximum hydrostatic pressure in the osmometer noticeably.

Experiment 1.—The osmometer was filled with a solution of sodium chloride, 0.1425 g-mol in a liter, and immersed in a sink trough filled with water. No stirrer was used this time. The temperature in the osmometer varied from 26°C to 26.6°C. The maximum hydrostatic pressure was found to be 122 cm of water column. The final concentration of sodium chloride in the osmometer was found to be 0.1298 g-mol. The theoretical osmotic pressure of this solution (calculated according to the formula $P = iRCT$) is 5795 cm of water column.

Experiment 2.—The above experiment was repeated but modified. The osmometer was filled with the solution of sodium chloride of the same concentration, and the maximum hydrostatic pressure found was 110 cm. Then a strong current of water from a glass tube (diameter 1.5 cm) was directed on the membrane of the osmometer from below. This current gave 12 liters of water in one minute. The distance between the tube opening and the membrane was 4 cm. When directed toward water surface the current gave a water jet of about one meter above the surface. The temperature in the osmometer varied from 25.5 to 26.1°C. In about 50 minutes the maximum hydrostatic pressure in the osmometer increased to 116 cm. This increase might result from a decrease of the stretching of the membrane. After the water current was stopped the maximum hydrostatic pressure decreased again, and it was found to be 109 cm. The final concentration of sodium chloride was found to be 0.1250 g-mol. The corresponding theoretical osmotic pressure is 5580 cm.

Experiment 3.—The concentration of the solution of sodium chloride in the osmometer was 0.0669 g-mol in a liter. The maximum hydrostatic pressure found was 53 cm. After a water current of 180 liters an hour was conducted into the trough at a distance of 20 cm from the osmometer the maximum hydrostatic pressure in the latter increased to 54 cm. Then the water current was directed on the membrane from below. In one hour the pressure was found to be 59 cm. The final concentration of the solution in the osmometer was 0.0645 g-mol. The theoretic osmotic pressure corresponding to this concentration is 3173 cm of water column. Temperature variations in the osmometer did not surpass 0.4°C.

From the experiments cited we may conclude that the removal of solute from the lower surface of the membrane does not affect noticeably the maximum hydrostatic pressure in the osmometer. Thus, the accumulation of the solute under the membrane is not responsible for the low pressure in the osmometer. It is evident that the penetration of the solute through the membrane affects this pressure in some other way. We may try now to elucidate this way.

Theoretical Aspect of the Problem

It should be emphasized that the problem of the dependence of the maximum hydrostatic pressure in the osmometer upon the permeability of the membrane should be distinguished from that of the dependence of osmotic pressure upon this permeability. We may consider first the latter problem. This problem seems at first incomprehensible because one defines osmotic pressure as a thermodynamic value independent of any membrane. If we define it, however, as a force necessary to separate solvent from solute, as Nernst does[6] and if we try to separate the former from the latter by means of a membrane, we will find that this force is greater in the case of a complete impermeability of the membrane to solute than in the case of its permeability. Indeed, a membrane which is permeable to solute can not separate the solvent from the solute completely. Also from the standpoint of the kinetic theory of osmotic pressure is the influence of the permeability of a membrane to solute on osmotic pressure comprehensible. Indeed, the osmotic pressure which can be considered from this standpoint as a sum of strikes on the membrane produced by molecules of solute is evidently greater if all molecules moving toward the membrane strike it than is the case when some of these molecules do not strike the membrane but penetrate through it, and this independent of whether the penetrating substance accumulates on the other side of the membrane or not.

Should we define osmotic pressure as a force which causes the solvent to penetrate into the solution through the membrane or as a force preventing this penetration, we will find that this force is smaller in the case of a permeable than of an impermeable membrane because this force results from the difference in concentration of the solute on two boundaries of the membrane and this difference is smaller when the solute penetrates the membrane. Even if we continuously replace the solution accumulating under the membrane by pure solvent, the force causing the solvent to pass into the solution through the membrane will be smaller because the layer of the solution adjacent to the membrane would always have a smaller concentration than that of the whole solution. Another question is whether such an incomplete force could be called osmotic pressure.

We may propose to call osmotic pressure, as it is usually done, a force necessary for a complete separation of the solvent from the solute, or resulting from a molecular bombardment of full strength, or necessary to prevent the passing of the solvent through the membrane when the latter is completely impermeable to the solute. We will call, however, the reduced force resulting from a certain permeability of the membrane to the solute *suction force of the solution.* We may try now to find the dependence of this force upon the permeability of the membrane to the solute. Let us suppose we have a cylindric vessel closed at both ends in which a piston made of a semipermeable membrane separates a solvent from a solution of a substance in the same solvent. We now move the piston in the direction of the solution so that the volume of the latter is diminished by a very small value Δv while the solvent passes from the solution through the piston on its other side. We produce a work equal to $P \Delta v$ where P is the osmotic pressure of the solution. If the

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[6] Nernst, W.: "Theoretical Chemistry," English transl. by L. Codd, 136 (1923).

piston is permeable not only to the solvent but also to the solute, this work is smaller than $P \Delta v$ because not the whole solute contained in the volume Δv is separated from the solvent. If the solute penetrates during the movement of the piston in such an amount through the latter that it would form a solution in the volume Δv of the solvent which has an osmotic pressure p, the work we produce by the movement of the piston is equal to $P \Delta v - p \Delta v$. As the rate of diffusion of the solute through the piston can be supposed to be proportional to the osmotic pressure P and to the permeability of the membrane to the solute, the osmotic pressure p is proportional to both. If μ is a number proportional to the permeability of the membrane to the solute, we can conclude that the work done is equal to $P \Delta v - \mu P \Delta v$ or $P(1 - \mu)\Delta v$. The force with which this work is done is equal to $P(1 - \mu)$, and this force is evidently the suction force of the solution at the membrane of which the piston is made. The work done by the movement of the piston is evidently independent of the permeability of the latter to water, because we can move the piston with a desirable speed, and the work done remains the same. We may write therefore $P_o = P(1 - \mu)$ where P_o is the suction force of the solution, P is the osmotic pressure of the solution and μ is a number proportional to the permeability of the membrane to the solute.

A similar formula expressing the dependence of the suction force of the solution can be deduced from Tammann's formula mentioned in the introduction. Indeed, if M is a number proportional to the permeability, we may write: $(P - P_b)/2P = M$ or $P_b = P(1 - 2M)$. This formula expresses, however, the hydrostatic pressure in the osmometer only in the case when the permeability of the membrane to solvent is so great that the penetration of the solute through the membrane producing a change of the volume of the liquid in the osmometer can be disregarded. In order to get an exact idea about the maximum hydrostatic pressure in the osmometer one should consider with v. Antropoff that this pressure results from the entering of the solvent into the osmometer and that the increase of the volume of the liquid in the latter is diminished by the exosmosis of the solute. It is evident, however, that v. Antropoff's "treibende Kraft der Osmose" is really the suction force of the solution. Thus P in his formula is equal to $P(1 - \mu)$ where P is the osmotic pressure of the solution, and the formula expressing the dependence of the maximum hydrostatic pressure P_m in the osmometer should be written as follows:

$$P_m = P(1 - \mu)(1 - \mu/\sigma)$$

In this formula μ is a number proportional to the permeability of the membrane to the solute, σ is proportional to that to the solvent, and P is the osmotic pressure of the solution in the osmometer. We may call μ and σ permeability factors for solute and solvent. It should be emphasized that this formula concerns the case when the solvent under the membrane into which the solute diffuses from the osmometer, is continuously renewed. If the membrane is both sides in touch with a solution, the formula should be written as follows: $P_m = [P_a(1 - \mu/\sigma) - P_b](1 - \mu)$ where P_a is the osmotic pressure of the solution inside, and P_b is that of the solution outside the osmometer. We are now going to test this formula on parchment paper. But in its application to the experiments described below one can simplify it. Namely, the volume of water into which the osmosis of the solute took place was in these experiments about 170 times greater than that of the solution in the osmometer, and the concentration of the solute in the outer liquid was at the end of the experiment in most cases more than 500 times smaller than that in the osmometer. Thus, without committing an error which surpasses the error unavoidable in the determination of the maximum hydrostatic pressure in the osmometer, we may omit P_b in the formula and test the formula: $P_m = P(1 - \mu)(1 - \mu/\sigma)$.

Dependence of the Maximum Hydrostatic Pressure upon Osmotic Pressure

From the above formula it follows that the ratio P_m/P should be constant if the permeability of parchment paper to water and sodium chloride is independent of the concentration of the latter. We may try whether this ratio is really constant.

The osmometer filled with a solution of sodium chloride (the concentration is given in Table I) was suspended above the water surface of the thermostat bath in a water vapor saturated atmosphere for three hours while the pressure in the osmometer was raised to a height corresponding to the maximum hydrostatic pressure found in a preliminary experiment. One could avoid in this way a too long osmosis of the solute and at the same time produce the necessary stretching of the membrane. After the indicated period of time the osmometer was immersed in water, and the determination of the maximum hydrostatic pressure could begin at once. The results are given in Table I, where C is the concentration of sodium chloride immediately after the determination of the maximum pressure expressed in g-mol in a liter, P is osmotic pressure corresponding to this concentration and P_m is the maximum hydrostatic pressure in the osmometer, both expressed in cm. of water column.

TABLE I

Maximum Hydrostatic Pressure P_m as compared to Osmotic Pressure.
Sodium Chloride. Parchment Paper

C	0.475	0.290	0.177	0.135	0.088
P_m	502	367	278	233	144
P	20910	13050	8120	6240	4110
P_m/P	0.024	0.028	0.034	0.036	0.035
C	0.067	0.050	0.029	0.026	0.016
P_m	122	97	62	59	39
P	3150	2370	1390	1250	770
P_m/P	0.035	0.040	0.045	0.047	0.050

From the results cited above we may conclude that the ratio P_m/P is approximately constant at the concentrations ranging from about 0.06 to 0.3 g-mol, but increases with a further decrease of the concentration. This may show that the permeability of parchment paper is constant at middle concentrations, but changes at the extremes.

In the experiments just described the membrane of parchment paper used was an old one, that is, it was used for filtration of water and salt solutions for three months. Such a filtration increases the permeability of parchment paper to water as well as to sodium chloride. The data concerning a fresh membrane of the same parchment paper will be revealed later.

Determination of Permeability Factors

In order to determine the permeability factors μ and σ the maximum hydrostatic pressure was determined for an ordinary membrane of parchment paper and for a double layer membrane of the same paper. The latter was made of two sheets of parchment paper stuck together with potato starch paste. The membranes were used for a filtration of water only for some days. After the maximum hydrostatic pressure in the osmometer had been determined, the same osmometer was used for the determination of the filtration rate of water and for the estimation of constants of the diffusion of sodium chloride through the membranes. The former, divided by the pressure used for the filtration gives the permeability of the membranes to water, while the diffusion constant gives the permeability of the latter to sodium chloride.

After the maximum hydrostatic pressure was determined, using one of the above membranes, the osmometer was filled with the solution of sodium chloride of a similar concentration but it was not connected with the capillary tube: it was closed with a rubber stopper through one of whose two openings a stirrer was introduced into the osmometer, while through the second opening a graduated glass tube was inserted bent horizontally in its outer part. This tube served for measuring of the volume of water sucked into the osmometer during the experiment. After a period of time indicated in tables during which the osmometer was immersed in the water of the bath the concentration of the solution in the osmometer was determined again. The concentration changes not only because sodium chloride diffuses through the membrane but also because water is sucked into the osmometer, and the concentration found by titration should be therefore corrected. The volume of the osmometer was 289 cc. If n cc of water were sucked into the osmometer, the corrected concentration is $1 + n/289$ times greater than the found one. The diffusion of sodium chloride through the membrane proceeded directly in the water of the thermostat bath. The volume of the latter was 170 times greater than that of the osmometer, the water in both was continuously stirred, and the concentration of sodium chloride in the bath at the end of experiments was not greater than 0.0005 g-mol in a liter. Thus, this concentration was simply substracted from the final concentration of sodium chloride in the osmometer. The diffusion constant K was calculated according to Fick's formula: $dS/dt = -KQ\,dC/dt$, which in our case takes the form: $VdC/dt = -KQC$, where V is the volume of the osmometer, C the changable concentration of sodium chloride in the latter, t is time period, and Q is the area of the membrane. After the integration we have: $K = (\log C_0 - \log C)/Qt$ where C_0 is the initial concentration, C the final concentration of sodium chloride in the osmometer. K is expressed in tables in g-mol passing through one sq. cm. of the membrane in one hour. The maximum hydrostatic pressure in the osmometer was determined for each membrane for three concentrations of sodium chloride, while the diffusion constant was found for two middle concentrations. The results are given in Tables II and III.

Concerning the permeability of both membranes to water, it was determined in the following manner. The osmometer was washed, filled with water and connected with the capillary tube as it was done in the case of the determination of the maximum hydrostatic pressure, but the capillary tube was filled with water. Then the osmometer was immersed in the water of the thermostat bath and the pressure in it was raised to 100 cm of water column. After three days of the filtration of water through the membrane under this pressure the rate of filtration was determined. It was found that this rate expressed in cc of water passing through one sq. cm. of the membrane during one hour is for the ordinary membrane equal to 215×10^{-5} and for the double layer membrane to 115×10^{-5}. This result is in accord with the supposition that the filtration rate is inversely proportional to the membrane thickness (Manegold and Hofmann.[7] The permeability of the membranes to water is accordingly 215×10^{-7} and 115×10^{-7}.

TABLE II

Maximum hydrostatic pressure P_m (cm of water column) as compared to osmotic pressure P. I for the ordinary membrane, II for the double layer membrane. C is the final concentration of sodium chloride in the osmometer (g-mol in a liter).

	I. Ordinary membrane			II. Double layer membrane		
C	0.124	0.071	0.035	0.122	0.072	0.033
P_m	111	60	39	218	120	81
P	5750	3340	1670	5650	3400	1580
P_m/P	0.019	0.018	0.023	0.039	0.035	0.051

TABLE III

Constant K of the diffusion of sodium chloride through the ordinary and double layer membrane. C_0 is the initial concentration, C is the corrected final concentration of sodium chloride. T is the time period during which the diffusion took place, in hours.

	I. Ordinary membrane		II. Double layer membrane	
C_0	0.1355	0.0629	0.1360	0.0705
C	0.1271	0.0589	0.1276	0.0636
T	2	2.03	4	6.73
K	0.0724	0.0720	0.0360	0.0345

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[7] E. Manegold and R. Hofmann: Kolloid-Z., 49, 372 (1929); 50, 22 (1930).

From these results we may conclude that the decrease of the permeability of the membrane used to water and sodium chloride approximately two times brings about the increase of the hydrostatic pressure in the osmometer two times. We may write, therefore: $2 = \frac{(1-\frac{\mu}{2})(1-\frac{2\mu}{2\sigma})}{(1-\mu)(1-\frac{\mu}{\sigma})}$ or $\mu = 0.66$. Considering now that the ratio P_m/P in the case of the ordinary membrane is equal at an average to 0.02 we may conclude that: $0.02 = 0.33\,(1 - 0.67/\sigma)$, or $\sigma = 0.71$.

Test of the Formula

Comparing the data given in Tables I and II we may conclude that the ratio P_m/P in the case of the membrane used for the data of Table I is greater than that of the membrane used for the data of Table II. As it was mentioned before, the first membrane was an old one through which water and salt solutions were filtered for three months while the second membrane was fresh and used for filtration only for some days. The difference in the ratio P_m/P is evidently explained by the fact mentioned before that prolonged filtration increases the permeability of parchment paper to water and sodium chloride. It was interesting to find both permeabilities for the membrane of Table I and to calculate according to the so obtained data the ratio P_m/P which should be similar to the same ratio found by the experiments if the formula expressing the dependence of the maximum hydrostatic pressure upon the permeability is correct.

The data concerning the diffusion constant of sodium chloride are given in Table IV.

Table IV

Constant K of the diffusion of sodium chloride through the membrane of parchment paper through which water had been filtered during three months. C_0 the initial concentration, C the final concentration (g-mol). T is time period during which the diffusion took place.

C_0	0.1525	0.0970	0.0490	0.0258
C	0.1431	0.0895	0.0443	0.0222
T	1.5	2	2.48	3.17
K	0.0930	0.0910	0.0908	0.0801

We see therefore that the diffusion constant for the membrane of Table I is at an average 0.0887, while for the membrane of Table II this constant is 0.0722. In other words, a prolonged filtration increased the permeability of the membrane for sodium chloride 1.23 times. The permeability to water was found to be also increased. For the membrane of Table I it was found to be 310×10^{-7} while this permeability for the membrane of Table II is, as it was mentioned before, 215×10^{-7}, that is, 1.44 times smaller. The ratio P_m/P for the membrane of Table I may be calculated therefore from the following equation:

$$P_m/P = (1 - 1.23\,\mu)\left(1 - \frac{1.23\,\mu}{1.44\,\sigma}\right), \text{ where } \mu = 0.67 \text{ and } \sigma = 0.71 \text{ or } P_m/P = 0.034.$$

The found ratio is very near the ratio found by the experiments for the membrane of Table I. Namely, it is at an average 0.037 (see Table I).

We may conclude therefore that the formula expressing the dependence of maximum hydrostatic pressure upon the permeability of a membrane found theoretically is confirmed by these experiments.

In order to test the formula for different concentrations of sodium chloride at which the ratio P_m/P was found to be different the membrane of Table I was used not only for the determination of the diffusion constant but also of the permeability to water at different concentrations of sodium chloride, Brukner[8] observed an increase of the filtration rate by addition of sodium chloride to water while the increase produced by weaker concentrations was found to be greater than that produced by strong concentrations. In the present experiments the osmometer was placed in a metal box covered inside with wet filter paper to prevent evaporation from the surface of the membrane, and after it was filled with a solution of sodium chloride the filtration rate was determined. It was found that, indeed, the filtration rate was greater than that in the case when water was filtered through the membrane, but between 0.04 and 0.15 g-mol it does not vary distinctly. We may assume therefore that it is constant at this concentration range. At concentrations which were lower than 0.04 g-mol the permeability decreased, however by about ten percent. In Table V are given the results. In this table C is the concentration of sodium chloride (g-mol), P is osmotic pressure in cm. of water column, K is diffusion constant, P_m is the maximum hydrostatic pressure experimentally found, P_m' the same pressure but calculated according to the formula $P_m = P(1 - \mu)(1 - \mu/\sigma)$ where μ is supposed to be proportional to K, and σ is proportional to the permeability of the membrane to water at different concentrations. As it was found above at concentrations ranging from 0.07 to 0.08 g-mol μ is equal to 0.82 and σ is equal to 1.02.

TABLE V

Maximum Hydrostatic Pressure experimentally found and calculated

C	P	K	μ	P_m (exp. f.)	P_m' (calc.)
0.159	7310	0.093	0.84	254	206
0.106	4930	0.092	0.83	179	155
0.071	3320	0.091	0.82	119	117
0.053	2520	0.091	0.82	95	89
0.029	1390	0.082	0.74	62	52

Considering the fact that μ and σ in the above formula were calculated approximately we may conclude from the results cited that this formula is confirmed by the experiments in a satisfactory degree.

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[8] Brukner: Z. Ver. deutsch. Zuckerind., **72**, 3 (1926).

Outlook on the Further Application of the Formula

In the experiments presented in the preceding chapters one and the same sort of parchment paper was used for the membrane. One can not doubt that it will be found correct also for other membranes. It should be emphasized, however, that μ and σ in the formula expressing the dependence of the hydrostatic pressure in the osmometer upon the permeability of the membrane should be determined for every membrane separately because the coefficients of proportionality between them and the permeability can be expected to be different. Some experiments made on two different sorts of parchment paper showed, for instance, that the diffusion coefficient of sodium chloride can be three to four times greater than in the case of parchment used in the experiments described above. It is evident that μ for these sorts of parchment paper can not be three or four times greater than it was found in these experiments. Otherwise the osmotic force of the membranes would be a negative value which is impossible.

On the other hand, the ratio μ/σ was near one for the membrane of parchment paper used in these experiments, because the exosmosis of sodium chloride from the osmometer into water expressed in grams through 1 sq. cm. was about one to one and a half times less than the endosmosis of water into the osmometer. If this ratio decreases, the hydrostatic pressure in the osmometer increases, and if the permeability of a membrane to water is very great in comparison with that to solute, the formula is practically transformed to: $P_m = P(1 - \mu)$. Such a case is evidently observed on the precipitation membrane of copper ferricyanide. Indeed, Tammann's experiments showed that the values μ calculated from Pfeffer's experiments in supposition that $P_m = P(1 - \mu)$ is proportional to the constant of the diffusion through this membrane.[9] The same case is also observed on living protoplasm which moreover possess a very small permeability factor μ so that the osmotic pressure which develops inside of the cells is near the theoretic value of osmotic pressure.

Summary

1. A too low hydrostatic pressure observed in an osmometer in which parchment paper is used as a membrane is not due to an accumulation of the solute (sodium chloride) under the membrane. The pressure which is about thirty times smaller than the theoretic osmotic pressure corresponding to the concentration of sodium chloride in the osmometer is increased very little when a water current giving 12 liters in one minute is directed on the membrane from below.

2. The force with which a membrane sucks water into an osmometer depends upon the permeability of the membrane to solute (sodium chloride). This dependence can be expressed by the formula $P_o = P(1 - \mu)$ where P_o is the *suction force of the solution*, P is its osmotic pressure and μ is the permeability factor proportional to the permeability of the membrane to solute.

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[9] Here μ is substituted for γ/nv of his formula.

3. The maximum hydrostatic pressure in the osmometer depends in general not only upon the permeability of a membrane to solute but also to its permeability to water. This dependence can be expressed by the formula: $P_m = P(1 - \mu)(1 - \mu/\sigma)$ where P_m is the maximum hydrostatic pressure, and σ is the permeability factor proportional to the permeability of the membrane to water. In the case of a copper-ferricyanide membrâne the formula of paragraph 2 is practically valid for the maximum hydrostatic pressure in the osmometer because the permeability to water is much greater in this case than the permeability to the solute (Tammann).

4. The factor of permeability as calculated from the experiments described in this paper for one kind of parchment paper and sodium chloride are equal: $\mu = 0.67$ and $\sigma = 0.71$. If the same parchment paper was used for filtration of water and salt solutions during three months, these factors became $\mu = 0.83$ and $\sigma = 1.02$.

AN UNUSUAL CRYSTAL GROWTH[1]

BY H. G. TANNER

A very peculiar crystal growth was observed when an attempt was being made to coordinate aniline with aluminum nitrate. Nineteen grams of aluminum nitrate nonahydrate (0.05 mole) was dissolved in sixty cc. of methanol. The solution was cooled with ice water, and to it was added with stirring fourteen grams of aniline (0.15 mole). A gel was formed which underwent partial syneresis rapidly. The initial exudate was removed by filtration on a Buchner. The gel was transferred with minimum disturbance to a piece of paper, and exposed to the air. From the gel grew a large tuft of white, lustrous, hair-like crystals shown by the accompanying photograph. The growth continued over a period of twenty-four hours. In one experiment the crystals attained a length of twenty-five centimeters.

FIG. 1

The crystals were analyzed and found to be aniline nitrate containing a trace of aluminum. The aluminum was present as a mechanical occlusion rather than a chemical constituent of the crystals.

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[1] Contribution No. 101 from the Experimental Station, E. I. du Pont de Nemours & Co.

Gels prepared with double the proportion of aniline behaved similarly, but a smaller quantity of aniline stunted the crystal growth. With the exception of ferric nitrate, no other salt was found to behave with aniline as did the aluminum nitrate.

The gel, as prepared by the above described procedure, was translucent because of the numerous bubbles and cracks developed by the agitation and filtration. This condition favors the formation of a larger "flower" of crystals, but renders difficult the microscopic observation of the mechanism which operates to form this peculiar type of growth. For the latter purpose a gel was prepared in a slightly different manner. The solution of aluminum nitrate was prepared as before, but cooled to −25° before adding the aniline. The low temperature permitted mixing of the aniline with the salt solution without apparent reaction. After the aniline had been added, the mixture was allowed to warm up to room temperature. Upon standing a few minutes it set to a nearly clear gel. Alcohol evaporated, of course, from the surface of this gel, and tiny crystals of aniline nitrate made their appearance. These were watched with a low-power microscope. They did not grow continuously, as would be expected, but spasmodically. When a crystal attained a certain size, which differed for individual crystals, the gel suddenly shrank away from the sides of the crystal. Any further growth therefore had to occur on the bottom face. In some manner, not understood, growth on the bottom forced the crystal upward. A height of six or seven centimeters above the surface of the gel was frequently attained by these crystals.

BERYLLIUM

IV. Micro Qualitative Analysis of Beryllium*

BY HAROLD SIMMONS BOOTH AND SPENCER GUILD FRARY

Introduction

Beryllium, although discovered in 1793 by Vauquelin and first prepared by Wöhler in 1828, has not shown much possibility of commercial importance until quite recently. However the demands of industry for light, strong alloys for aircraft and highly specialized alloys for other purposes will probably increase manufacturing of the metal and bring the price down to the point where it can be profitably employed.[22]

Beryllium is not a rare element and in certain localities is rather abundant. Washington[25] states that "beryllia has never, so far as I know, been determined in the analysis of an igneous rock. Yet the fact that the aluminosilicate, beryl, is not a rare mineral indicates that beryllium is fairly widespread. Beryl occurs in granitic and syenitic pegmatites, especially sodic ones. It is also found in metamorphic rocks. It has been suggested that in some cases beryllia has been weighed with, and supposed to be alumina, unidentified beryl being present, thus accounting for an apparent excess of Al_2O_3, which it is difficult to reconcile with the mineral composition of the rock. It has been shown recently that alumina has been mistaken for beryllia in the mineral vesuvianite,[20] in which the presence of beryllium had not been suspected. The need of a closer study of some minerals and rocks as regards this point is obvious. It might be well to determine BeO in granites associated with beryl-bearing pegmatites and in some nephelite syenites."

In a more recent article Washington[24] again stresses the importance of analyzing silicate minerals and igneous rocks for beryllium. Barylite was found to contain beryllium in place of the aluminum hitherto supposed to be present.

Because of its low atomic weight the percentage of beryllium in most minerals is not very great; beryl, the most common, contains only 4 to 5 per cent beryllium as the metal. Since beryl is the present commercial source of the element despite a hardness of 7.5 to 8 and the natural difficulty of decomposing silicates which make it far from satisfactory, it is of interest to know if there are other sources of the element that might prove of value.

To prevent the element from being overlooked in the future it is important that the methods of its detection be improved, if possible. To this end a study of the microqualitative detection of beryllium has been made.

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*Contribution from the Morley Chemical Laboratory, Western Reserve University. For Beryllium I, II, and III see J. Phys. Chem., 35, 2465, 2492, 3111 (1931).

Historical

Beryllium at the head of group II of the periodic table has many of the chemical characteristics of aluminum in group III. The two hydroxides closely resemble each other and it is their separation that offers the chief difficulty in quantitative analysis. In the ordinary course of analysis they are precipitated together and weighed as alumina.

There have been many separations suggested for beryllium and aluminum. Of these methods, Britton[2] found that the best were:

1. Decomposition of sodium beryllate solutions by boiling to precipitate beryllium hydroxide.[11]

2. Parsons and Barnes' method of momentarily boiling a saturated solution of sodium bicarbonate.[21]

3. Wunder and Wenger's method of fusing the oxides of beryllium and aluminum in sodium carbonate. Sodium aluminate is formed while the beryllia is unaffected.[26]

4. Haven's method in which a concentrated solution of the chlorides is treated with an equal volume of ether and dry hydrogen chloride gas passed in, to precipitate the aluminum chloride.[12]

Since that time a newer separation in which 8-hydroxyquinoline is used to precipitate the aluminum has been developed which is quite satisfactory for quantitative analysis.[16,17]

For the determination of small amounts of beryllium in large amounts of aluminum, a combination of the Havens, and 8-hydroxyquinoline methods has been suggested.[7] By this means most of the aluminum is removed first, avoiding the use of an excessive amount of the rather expensive 8-hydroxyquinoline.

In the analysis of minerals, Hills[14] recommends the use of Parsons' method of boiling a concentrated solution of sodium bicarbonate, followed by the 8-hydroxyquinoline separation to remove the last of the aluminum.

There are very few really distinctive qualitative tests for the detection of either beryllium or aluminum. H. Fischer[9] suggests the use of quinalizarin (1,2,3,8 tetrahydroxy anthraquinone alizarin bordeaux) for the detection of small amounts of beryllium and I. M. Kolthoff[15] suggests curcumin for the detection of the element. Both of these are adsorbed by beryllium hydroxide, giving characteristic colors.[13]

Microqualitative Methods of Analysis

Chemical microscopy, on the other hand, offers simple, easy methods of qualitative analysis in many cases where the ordinary methods are laborious and often inexact. In the case of beryllium there are several tests that distinguish it quite definitely from aluminum and other elements with which it might be associated.

A satisfactory microqualitative test should have the following characteristics: (1) the resulting product should have a large molecular weight in proportion to the amount of the element actually present; (2) a small amount of the substance should give a positive test; (3) the products formed should have characteristics that distinguish them from the reagent and from any other elements that might be present; (4) the test should give good results under not too rigid conditions; (5) the test should be comparatively simple and not involve too many steps; (6) the resulting products should have an index of refraction so different from the solution that they may be easily distinguished.

Double salts of beryllium should give good tests because of the low atomic weight of the element. For example, in the potassium oxalate test the double salt formed has a molecular weight of 263, of which only 9 parts are due to the beryllium present. Likewise in the chloroplatinic acid test the crystals obtained have the composition $BePtCl_6.8H_2O$, with a molecular weight of 560, only 9 parts of which are due to the element being detected.

The third requirement, that of characteristic properties of the products, is not so well met in the case of beryllium, due to the fact that so many of the insoluble compounds of beryllium separate as amorphous, basic salts that have no distinguishing characteristics. Since solutions of beryllium salts have the property of dissolving beryllium hydroxide and the salts also hydrolyze quite readily, it is, in many cases, difficult to get crystalline products of definite composition. This property probably accounts for many of the strange, unsubstantiated compounds found in the literature of beryllium.

Many reagents cause the precipitation of the hydroxide which in itself is useless as a microqualitative test for beryllium; though failure to obtain any hydroxide precipitate can be taken as a negative test showing the absence of the element. Or the precipitate can be filtered and dissolved in a small amount of acid thus concentrating it and increasing the accuracy of the test as well as effecting a separation from other material that might interfere.

Precipitation with ammonia and filtration through a microfilter, or careful evaporation of the test drop, will show amounts of the hydroxide down to 0.0007 mg. With smaller amounts a spectrographic analysis is the best means for the detection of beryllium.

Experimental

To determine the limit of accuracy of the various methods a procedure similar to that given by Chamot and Cole was used.[5] A series of four beryllium nitrate solutions were made up such that each was one-tenth the concentration of the previous one.

In order to be sure of getting the same amount of solution each time, micropipettes made by drawing out glass tubing to a capillary tip and attaching rubber bulbs to facilitate handling the solutions, were used. Measurements into a graduated cylinder showed the drops to average fifty to a cubic centimeter hence each contained 0.02 cc.

Gravimetric analysis of the first solution showed it to contain 3.3 mg. of beryllium per cubic centimeter, or 0.066 mg. per drop. The beryllium content per drop of the different solutions was:

No. 1	0.066 mg. beryllium per drop
No. 2	0.0066 mg. per drop
No. 3	0.00066 mg. per drop
No. 4	0.000066 mg. per drop

Most limits of accuracy are given in micro milligrams (μ mg.), equivalent to 0.001 mg. Expressed in this manner the four solutions would have the following beryllium content per drop: No. 1, 66.0μ mg.; No. 2, 6.6μ mg.; No. 3, 0.66μ mg. and No. 4, 0.066μ mg.

The textbooks on chemical microscopy[6,17,1] give the following methods for the detection of beryllium:

1. Reaction with potassium oxalate to form the double salt, beryllium potassium oxalate ($K_2C_2O_4.BeC_2O_4$).

2. Reaction with chloroplatinic acid to form beryllium chloroplatinate, ($BePtCl_6.8H_2O$).

3. Reaction with sodium and uranyl acetates to form the triple salt, sodium uranyl acetate, $Na(C_2H_3O_2).Be(C_2H_3O_2)_2.3UO(C_2H_3O_2)_2.9H_2O$.

All three of these books recommend the potassium oxalate method as the best for beryllium.

Beryllium Potassium Oxalate. $K_2C_2O_4.BeC_2O_4$.

Chamot[6] recommends a neutral, moderately concentrated test drop to which a little acetic acid is added; then the reagent is added in a fragment that, in this case, must be more than twice the size ordinarily used.

According to Chamot, "$K_2C_2O_4.BeC_2O_4$ separates in large, stout, clear, colorless, monoclinic prisms; single, in twins, or in groups of radiating, irregularly formed prisms. Thin plates in the form of rhombs are also obtained. The salt is strongly birefringent and exhibits an extinction angle of about 39°.

"Unless the reagent is present in sufficient excess the test is apt to prove unsatisfactory. Acid potassium oxalate or the oxalates of sodium or ammonium are not suitable reagents.

"During the disintegration and solution of the reagent fragment well-formed crystals of $K_2C_2O_4$ usually appear momentarily. These crystals often bear a striking resemblance to the double salt, and it is therefore imperative that the analyst shall be on his guard lest he fall into error through too hasty a decision."

Chamot adds that the double salt can be recrystallized by gently warming the slide and cooling, whereupon well-formed crystals are obtained.

Behrens[1] suggests the addition of a little mercuric chloride to cause the formation of elongated prisms, thus making it easier to distinguish the double salt from the reagent.

Lindsley[17] states that ammonium salts should be absent when testing for beryllium with potassium oxalate.

When this test was made according to Chamot[6] crystals were obtained with all the solutions. It was subsequently found that acetic acid in a drop of water gave similar crystals. Solutions of beryllium salts hydrolyze sufficiently to give the slight acidity necessary for the formation of the double salt so that the addition of acetic acid is unnecessary and should be avoided as it interferes with the test.

Behrens[1] gives 0.08 mg. as the limit of accuracy of the potassium oxalate method. This is the minimum amount of beryllium in a test drop that will give a positive test. This would correspond to slightly more than one drop of the No. 4 solution.

A positive test was obtained with the No. 3 solution equivalent to a limit of accuracy of 0.7μ mg.

Before arriving at these conclusions, several methods of obtaining the right acidity and at the same time avoiding ammonium salts were attempted. It was found, however, that ammonium salts did not interfere and that beryllium hydroxide, dissolved in a little hydrochloric or sulfuric acid, or solutions of the salts, could be used for the test without any preliminary treatment.

Very dilute solutions can be concentrated by gentle evaporation and highly acidic solutions had best be neutralized with ammonia and the precipitated hydroxide dissolved in acid.

Aluminum, ferric iron and chromium gave no crystals with the reagent. They are the elements most likely to be present in the ordinary course of analysis.

Adding mercuric chloride to the solution made no appreciable change in the shape of the crystals obtained and appeared to interfere with the test to some extent.

Beryllium Chloroplatinate, $BePtCl_6.8H_2O$.

This test is performed by evaporating the test drop to a nearly dry film and then drawing the concentrated reagent solution across the film in a narrow channel. Beryllium chloroplatinate separates out in hydroscopic, faintly yellow, square and rectangular plates, usually singly, but sometimes penetration twins are formed. Chamot[6] says that the formation of the crystals can be induced by the addition of alcohol.

The precipitate should be examined with crossed nicols. The beryllium salt exhibits parallel extinction and is only weakly birefringent. As the alkali metals form characteristic crystals with chloroplatinic acid they should not be present in too great amounts.

Chamot states further that in his opinion this test is valueless unless the material is so high in beryllium as to constitute a fairly pure salt.

When this test was first tried no crystals were obtained due to the reagent solution being too dilute; after evaporating it down to a thick sirup good results were obtained with the No. 3 solution. Therefore, the limit of accuracy was found to be 0.7μ mg.

However, the addition of alcohol recommended by Chamot caused everything to dissolve and spoiled all the crystals rather than aiding in their formation.

Aluminum did not interfere with this test and it is probable that, if the beryllium and aluminum were precipitated as the hydroxides and washed free from everything else, except possibly a slight trace of ammonium salts, this test would work reasonably well.

Sodium Beryllium Uranyl Acetate.

Beryllium is supposed to form a triple salt with sodium and uranyl acetates similar to those formed by magnesium and zinc. This method is mentioned by Caglioti[3] as a test for beryllium but neither Miholic[19] nor Bedient[4] were able to obtain the triple acetate unless the solution went to dryness.

When this test was tried no crystals were obtained that could be used as a test for beryllium. It seemed impossible to get the salts to crystallize unless the solution was evaporated almost to dryness.

Caglioti[3] also suggests the acetyl acetone derivative prepared by treating acetyl acetone with beryllium acetate solution, slightly acidified with acetic acid. Monoclinic tablets, or thin prisms, are supposed to be obtained by slow crystallization. Caglioti states that this is preferable to the triple acetate as a microqualitative test for beryllium.

This test recommended by Caglioti was also attempted but no crystals were obtained. On one occasion some crystals were observed but, on repeating the test under apparently the same conditions the crystals failed to reappear.

Search for New Reagents

With the hope of finding a reagent better than potassium oxalate for the microqualitative analysis of beryllium, many substances which give distinctive tests, with other elements, were tried with beryllium salts.

Since the great majority of these failed to give any definite reactions with beryllium the results are only briefly given in tabular form.

TABLE I

Reactions of several organic compounds with beryllium nitrate solutions, first alone, then with KCNS, and finally with KCNS in acid solution were investigated, and also those with aluminum chloride were tried to determine what effect it would have as an impurity.

Reagent	Beryllium nitrate	Aluminum Chloride
Acridine	No action alone. Reacted with KCNS to give crystals	No action
Resorcine	No action	No action
Benzidine	No action; crystals of reagent on heating	No action
Diphenylamine	No action	No action
Phthalic anhydride	No action	No action
Picric acid	No action; crystals of reagent on heating	No action
Pyrogallic acid	No action; crystals of reagent on heating	No action
Uric acid	Reagent insoluble; no action	No action
Eosine	No action	No action
Fluorescene	No action	No action

TABLE II

Results of reactions of inorganic compounds on solutions of beryllium nitrate.

Potassium dichromate	No reaction
Potassium permanganate	No reaction
Potassium tartrate	No reaction
Potassium antimonate	Precipitated beryllium hydroxide
Sodium arsenate	Precipitated beryllium hydroxide
Sodium bismuthate	Precipitated beryllium hydroxide
Sodium nitrate	No reaction
Sodium phosphotungstate	White curdy precipitate
Sodium nitroprusside	No reaction
Sodium thiosulfate	No reaction
Disodium phosphate	White curdy precipitate
Ammonium persulfate	White curdy precipitate
Ammonium phosphomolybdate	Only soluble in alkaline solutions; beryllium hydroxide precipitates
Dimethylglyoxime	No reaction
Ammonium vanadate	Orange color and precipitate. (Aluminum gave a pale yellow color)
Ammonium fluostannate	No reaction (aluminum gave a precipitate)
Ammonium fluotitanate	No reaction (aluminum gave a precipitate)
Potassium fluoride	No reaction (aluminum gave a precipitate)
Potassium bifluoride	No reaction (etched the slide rapidly).

TABLE III

Beryllium hydroxide was dissolved in solutions of the following acids and evaporated.

Succinic acid	No reaction
Citric acid	No reaction
Tartaric acid	No reaction
Malonic acid	No reaction
Salicylic acid	No reaction
Cinnamic acid	Rectangular crystals
Benzoic acid	Needle crystals

The majority of the substances studied gave no particular reaction but there were a few that appeared to have interesting possibilities, that deserve a more detailed discussion.

The reaction of sodium fluoride and some of the fluo-salts with solutions of beryllium and aluminum salts is a means of distinguishing between them and has been proposed as a method of separation.[10]

Britton[2] states that this method is not quite quantitative due to the slight solubility of sodium aluminum fluoride. However, a sample of beryllium oxide made by the Copaux[6] process in which the separation is based on the insolubility of the sodium aluminum fluoride, showed little if any aluminum when examined spectrographically.

However, the use of fluorides under the microscope is rather objectionable as special precautions have to be observed to protect the lenses from corrosive fumes. Cover glasses can be fastened to the objective with cedarwood or Canada balsam, but even so there is danger of corrosion if used for any length of time.

Test with Potassium Malonate

Potassium malonate was studied because malonic acid is the second member of the series of organic acids of which oxalic is the first. As the potassium oxalate test is the best so far known for beryllium, it was of interest to determine if potassium malonate would give a similar reaction with solutions of beryllium salts.

A fragment of the salt was added to the test drop and the solution carefully evaporated. With more concentrated solutions, well shaped rhombs were formed at the edge of the drop. When these were pushed into the center and the evaporation continued, long monoclinic prisms were formed.

The rhombs, observed under polarized light, with crossed nicols, gave oblique extinction at an angle of 38°. The prisms showed parallel extinction.

The rhombs were obtained in a drop of the No. 1 solution; the No. 2 solution gave only the prisms. The limit of accuracy of this method would be 6.6μ mg.

Test forming Beryllium Basic Acetate

Beryllium is unique in forming a volatile basic acetate. This compound is prepared[23] by dissolving the hydroxide in acetic acid, evaporating the solution to a gummy mass, dissolving in glacial acetic acid, and boiling off the excess acid; on cooling the solution, the basic acetate separates out in the form of octahedral crystals.

While this method is not easily applicable to tiny amounts of unknown, if about a cubic centimeter of unknown solution is taken and the beryllium converted to the basic acetate, only a small amount of the resulting solution need be taken.

Although the absolute accuracy of this test is in the order of one milligram, this is more than compensated by the fact that the crystals obtained are highly refractive and quite characteristic.

The glacial acetic acid is very mobile and it is best to place the drop to be observed in a hollowed-out slide to prevent its spreading over the slide and evaporating too rapidly.

TABLE IV

The limit of accuracy of these methods:

Beryllium potassium oxalate	0.7μ mg.
Beryllium chloroplatinate	0.7μ mg.
Beryllium malonate	7.0μ mg.
Beryllium basic acetate	1000μ mg

Conclusions

The most satisfactory microqualitative test for beryllium so far found is the potassium oxalate method. It does not require any elaborate procedure and the sensitivity is more than sufficient for all practical purposes. The limit of accuracy is about 0.7μ mg. Contrary to the literature, acetic acid should be avoided and ammonium salts do not interfere.

The chloroplatinic acid test is suitable where the beryllium is not too contaminated with other material. In some cases the beryllium and aluminum can be separated from other material as the hydroxides, before applying the test. With pure beryllium solutions the limit of accuracy of this test is 0.7μ mg.

Potassium malonate can be used as a reagent for the detection of beryllium. The limit of accuracy is 7.0μ mg.

Beryllium basic acetate recrystallized from acetic acid can be used as a confirmatory test for the element though its limit of accuracy is only about one milligram.

The reactions of the fluorides can be used as a means of distinguishing beryllium from aluminum provided precautions are taken to protect the apparatus from fluoride fumes.

The above methods of microqualitative analysis offer the best means for the detection of beryllium. They are superior to the ordinary methods of qualitative analysis both in simplicity and in accuracy. If these methods are applied to the precipitated hydroxides ordinarily obtained in macro qualitative analysis, they should show conclusively the presence of any hitherto unsuspected beryllium.

Summary

1. The application of the methods of chemical microscopy to the qualitative analysis of beryllium was studied.

2. A study was first made of the present method to determine their limitations and advantages.

The potassium oxalate method was found to be the most satisfactory.

The chloroplatinic acid method was found satisfactory under certain conditions.

3. An attempt was made to find new methods that would supplement or replace the present ones.

4. As a result of this investigation two methods are proposed:

The use of potassium malonate in a manner similar to potassium oxalate.

The use of the basic acetate recrystallized from glacial acetic acid as a confirmatory test.

5. The above micro methods are believed to be superior to the macro qualitative methods, as a means of identification of beryllium, especially if applied to the precipitate of aluminum and beryllium hydroxides, as ordinarily obtained in macro qualitative separations.

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NITROGEN COMPOUNDS OF GALLIUM
III. Gallic Nitride*

BY WARREN C. JOHNSON, JAMES B. PARSONS AND M. C. CREW

Introduction

A nitride of each member of Family B, Group III, of the periodic system with the exception of gallium has been reported in the literature. Boron nitride has been prepared by several different methods. Stock and Blix[1] obtained the nitride by the decomposition of boron imide; Meyer and Zappner[2] passed a mixture of boron trichloride and ammonia through a tube heated at high temperatures and obtained boron nitride of high purity; and Friederich and Sittig[3] have reported the formation of the compound through the direct combination of its elements at 1200°. It is described by several workers as an exceedingly stable compound. Aluminium has been shown to combine directly with nitrogen[4] to form a nitride of definite composition. The nitrides of indium and thallium have been reported by Fischer and Schroter.[5] They employed the discharge of an electric arc through a mixture of liquid argon and liquid nitrogen, with the metal serving as electrodes, to cause combination of the elements. In each case a black powder was obtained which appeared to be quite unstable thermally, even at very low temperatures. The data available at the present time are not sufficient, however, to warrant the existence of indic and thallic nitrides as definite compounds. On the other hand, Franklin[6] has been successful in the preparation of thallous nitride, Tl_3N, in liquid ammonia solution from thallous nitrate and potassium amide.

In view of the position of gallium in third group of elements, one would predict the formation of a nitride possessing properties similar to those of the nitrides of aluminium and indium. The following report shows that gallic nitride resembles aluminium nitride and boron nitride in its apparent stability towards heat, solutions of acids and of bases.

Experimental

Metallic gallium was obtained from germanite ore according to a procedure previously described.[7] It was purified by fractional crystallization on a platinum wire from the supercooled liquid metal.[8] Liquid ammonia was thoroughly dried with sodium before being used in any of the experiments.

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* Contribution from the George Herbert Jones Laboratory of the University of Chicago.

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Gallium nitride, GaN, was prepared by the action of ammonia gas on metallic gallium at high temperatures. A boat containing the metal was inserted in a Vitreosil tube which was heated by an electric furnace. The temperature was measured with a Pt,Pt-Rh thermocouple and a Leeds and Northrup Potentiometer Indicator. Reaction was found to proceed slowly at a temperature as low as 700°, but it was necessary to heat the metal to 900-1000° for several hours in order to obtain an amount of the nitride sufficient for analysis and study. This procedure was found to be disadvantageous in two respects; (1) metallic gallium is appreciably volatile at temperatures approaching 1000° and consequently distills out of the boat to condense in the cooler regions of the tube without reacting with the ammonia, and (2) the nitride also sublimes at these temperatures to leave the reaction mass. However, the higher temperatures were employed throughout the preparations to obtain appreciable quantities of the nitride although it was found impossible to determine the extent of a given reaction merely by the change in weight of the boat and contents.

When the reaction between metallic gallium and ammonia was completed, the product was analyzed for nitrogen by the distillation of ammonia from a concentrated NaOH solution. The results are shown in Table I under samples listed (1) and (2) which represent two different preparations of the compound. The nitrogen content obtained from the analyses suggests that one atom of gallium is in combination with one atom of nitrogen. The reaction may be expressed as follows:

$$2Ga + 2NH_3 = 2GaN + 3H_2. \qquad (1)$$

Table I

Analysis of Gallic Nitride for Gallium and Nitrogen

Sample	GaN, g.	Ga (found), g.	Ga (calcd.), g.	N_2 (found), g.	N_2 (calcd.), g
(1)	0.0689			0.0115	0.0115
(2)	.1802			.0299	.0301
(3)	.1207			.0209	.0202
(4)	.2070	0.1710	0.1724		
(5)	.2088	0.1746	0.1747		

In order to carry out an analysis of the nitride for nitrogen by the Kjeldahl method, concentrated NaOH solution was used to dissolve the compound. Dilute alkali appeared to have little effect on the nitride, and even the concentrated solution dissolved it slowly on heating. Attempts to recover the gallium from the solution, after the ammonia had been liberated, did not produce satisfactory results due to the presence of appreciable amounts of silica which had been removed from the glass. The possibility of reduction of the nitride at high temperatures with hydrogen to metallic gallium and ammonia was considered in view of the results previously obtained with germanic nitride.[9]

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[9] Johnson: J. Am. Chem. Soc., 52, 5160 (1930).

A small sample of the nitride, 0.1592 g, was heated in a stream of hydrogen at 800° for 24 hours. An examination of the material at the end of this period showed no change in its appearance but a loss in weight of 0.0385 g was noted. On the other hand, a considerable quantity of a grey substance resembling the nitride collected on the walls of the quartz tube outside the heated area. If the nitride were to be completely reduced to metallic gallium without any distillation, the loss in weight would be only 0.0266 g to correspond to the nitrogen. Accordingly, the material remaining in the boat was analyzed for nitrogen by the method indicated above. The results given in Table I (sample 3) show the material to be identical with gallic nitride. This conclusion is substantiated by the fact that the gases discharged from the reaction tube failed to produce any effect on a dilute HCl solution. Evidently, the nitride is slightly volatile at 800°, under a pressure of 1 atmos. of hydrogen, without suffering decomposition or reduction.

Two different methods were found applicable for the determination of gallium. In the first method, the nitride was dissolved in hot, concentrated H_2SO_4, the excess acid was evaporated, the residue dissolved in water, and the gallium was precipitated as hydroxide in the presence of NH_4HSO_3 according to the procedure described by Porter and Browning.[10] The hydroxide was ignited and finally weighed as Ga_2O_3. The gallium content is calculated and shown in Table I (sample 4).[11] The second method for the determination of gallium was accomplished by passing oxygen gas over the nitride at high temperatures to form gallic oxide according to the following expression:

$$4GaN + 3O_2 = 2Ga_2O_3 + 2N_2. \qquad (2)$$

The oxidation was found to proceed slowly even at temperatures approaching 900°. At 500° no reaction was observed while at 800° some gallic oxide was noticed after several hours heating. Approximately 30 hours at 875-900° were required to completely oxidize a 0.2 g sample of the nitride. Sublimation of the nitride was not noticed in this experiment; undoubtedly, the oxide which forms at the surface tends to prevent an escape of the more volatile material. The results of the oxidation are given in Table I (sample 5).

All attempts to react metallic gallium directly with nitrogen gas were unsuccessful. Nitrogen was passed over the metal at temperatures ranging from 500-1000° for several days but no indication of a combination of the two constituents was observed.[12]

Properties of Gallic Nitride. Gallic nitride is an exceedingly stable compound. Above 800° it sublimes without decomposition. It is not reduced with

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[10] Porter and Browning: J. Am. Chem. Soc., 41, 1491 (1919).

[11] No attempt was made here to determine the nitrogen of the nitride digested with the concentrated H_2SO_4. Undoubtedly, this procedure would allow for analysis of both nitrogen and gallium and thus eliminate the use of concentrated NaOH for the determination of nitrogen.

[12] Observations by Miss E. DeSylvester in this laboratory. Some gallic oxide was formed in this experiment due to traces of oxygen with the nitrogen which escaped removal in being passed over copper at 600°. However, the contents of the reaction chamber failed to show the presence of nitrogen when subjected to analysis.

hydrogen at 900°, but reacts slowly with oxygen at this temperature to form gallic oxide. The nitride is unchanged when treated with dilute and concentrated solutions of HCl, HF and HNO_3. Hot aqua regia has no effect on the nitride. The compound dissolves slowly in hot, concentrated H_2SO_4 and also in hot, concentrated NaOH. It is stable in air; a sample exposed to air for several weeks showed no change in weight or in appearance. The nitride, as prepared by the reaction between metallic gallium and ammonia gas at high temperatures, appears as a dark grey powder.

Summary

Gallic nitride, GaN, is prepared by reacting metallic gallium with ammonia gas at 900-1000°. Some of its properties are studied and discussed.

Chicago, Illinois.

THE INFLUENCE OF GASES ON THE NORMAL POTENTIAL OF THE ZINC ELECTRODE

BY FREDERICK H. GETMAN

In all modern precise determinations of normal electrode potentials it is customary to exclude air from the electrolyte and the electrode vessel. Hydrogen and nitrogen are the two gases most commonly employed for this purpose. In a recent study of the effect of different gases on the potential of the aluminium electrode, Kahlenberg and French[1] have shown that oxygen, hydrogen and nitrogen produce marked changes in the potential of the metal as measured in air-saturated solutions of potassium chloride. Both nitrogen and hydrogen were found to render the potential decidedly more basic, whereas with oxygen the potential was found to be less basic than when air alone was present. In a subsequent communication the same authors[2] studied the effect of carbon monoxide, methane and helium, in addition to the gases previously mentioned, on the potentials of a number of metals and concluded that the metals form "gas-metal" electrodes with gases, the potentials being specific for each particular metal and gas, and related to the absorbing power of the metal for the gas, and the affinity of the metal for each gas in the case of a mixture. The total combined potential is believed to be due both to absorbed gas and a condensed film of the gas on the surface of the metal. Those elements which have a tendency to form acids behave differently with oxygen than do the other elements. Amphoteric elements as well as those which exhibit variable valence, or function as catalysts, were found to show greater changes with hydrogen and nitrogen than do the more pronouncedly metallic elements.

Both methane and carbon monoxide were shown to produce very appreciable changes in the potentials of both platinum and palladium. Coating the electrodes with collodion, or stirring the electrolyte, prevented the condensation of a gas film on the surfaces of the electrodes. It was found that those electrodes which exhibited the smallest differences between their oxygen and nitrogen potentials were in every case the most constant. The authors concluded that the so-called single potentials of the metals, determined in air, are in reality "air-metal" electrodes, and consequently that the commonly accepted electrochemical series of the metals requires fundamental revision. Whereas in the foregoing investigations the authors had confined themselves to a single electrolyte, normal potassium chloride, in a continuation of the investigation by Kreuger and Kahlenberg,[3] the effects of oxygen, hydrogen, nitrogen, helium and argon on the potentials of all the common

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[1] Kahlenberg and French: Trans. Am. Electrochem. Soc., 52, 355 (1927).

[2] French and Kahlenberg: Trans. Am. Electrochem. Soc., 54, 163 (1928).

[3] Krueger and Kahlenberg: Trans. Am. Electrochem. Soc., 58, 107 (1930).

metals and carbon were studied in normal solutions of potassium chloride, potassium hydroxide and hydrochloric acid. It was found that the potentials of arsenic, natural graphite, cocoanut charcoal, cadmium, mercury, molybdenum, lead, silicon, tin, tantalum, tellurium, tungsten and zinc were only slightly altered by any of the gases, irrespective of which of the three electrolytes were used. The experimental data were interpreted as indicating that there is no such thing as a true gas electrode but that the so-called gas electrodes are to be regarded as "gas-metal" electrodes.

In discussing the results of the work of French and Kahlenberg, Blum[4] disagrees with the statement that fundamental revision of the entire electrochemical series is required. He points out that the commonly accepted values of the potentials of the metals have been determined not in a solution of potassium chloride but in solutions of salts of the respective metals, each salt on solution yielding ions of the metal in question. He stresses the fact that the respective values in the electrochemical series are not so much an indication of the potential in a particular solution, as they are a measure of the tendency of the metal to go into solution in the form of ions. He further emphasizes the fact that to obtain a strictly reproducible potential it is absolutely necessary to exclude the possibility of more than a single reaction taking place at the electrode. This condition clearly does not obtain when the electrode is immersed in a solution of a salt which on dissociation does not yield ions of the metal whose potential is sought.

In a careful study of the nickel electrode, Haring and Vanden Bosche[5] found that the potential of the metal was appreciably lowered by the presence of oxygen or air, and was correspondingly raised by the presence of hydrogen. In consequence of these facts they exercised special care to insure the exclusion of these gases in their final precise determinations of the electrode potential of nickel. The cell finally adopted by Haring and Vanden Bosche was the following

$$\mathrm{Ni,\ NiSO_4,\ Hg_2SO_4,\ Hg.}$$

This will be seen to involve no liquid junction and to be completely reversible with respect to the nickel ion. The effects of oxygen and hydrogen on the potential of nickel were found to be directly opposite to those previously observed by French and Kahlenberg with nickel electrodes in normal potassium chloride.

In view of the foregoing work, it seemed of interest to study further the influence of air, oxygen, hydrogen and nitrogen on the potential of zinc when immersed in a solution of a zinc salt. To this end the following cell was chosen:

$$\mathrm{Zn,\ ZnCl_2(m),\ KCl(0.1m),\ Hg_2Cl_2,\ Hg.}$$

Materials

The zinc electrodes used were in the form of single crystals formed from metal of a high degree of purity.

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[4] Blum: Trans. Am. Electrochem. Soc., 54, 193 (1928).

[5] Haring and Vanden Bosche: J. Phys. Chem., 33, 161 (1929).

The zinc chloride was prepared from Kahlbaum zinc by dissolving in pure hydrochloric acid. An excess of metal was added to the solution before concentrating, thereby minimizing acidity. When the solution had been evaporated to a syrupy consistency it was filtered through a column of pure zinc hydroxide into a liter flask where, after diluting with conductivity water, it was allowed to stand for a week or more. The molality of the solution was then determined by gravimetric estimation of the chloride ion as silver chloride, together with a measurement of its density by means of a pyknometer. The materials used in preparing the calomel electrode were of the high standard of purity specified for that purpose.

All gases used were obtained in pressure tanks and were found to be sufficiently pure after passing through appropriate saturators.

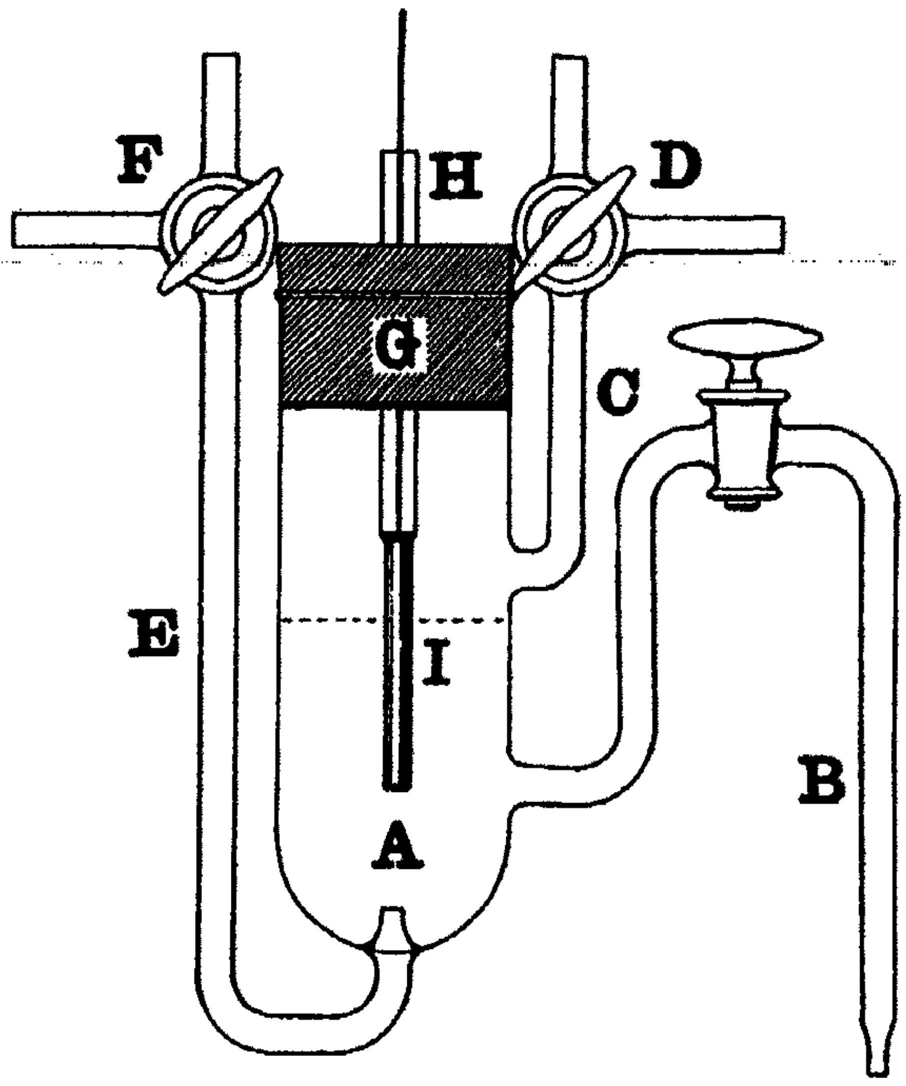

Fig. 1

Apparatus

A special electrode vessel, designed to facilitate the introduction and removal of both gases and electrolyte, was constructed of Pyrex, as shown in Fig. 1. Into the large tube A were sealed three side-tubes B, C and E. The tube B was furnished with a ground-glass stop-cock and served to connect the electrolyte, through a salt bridge of 0.1 m potassium chloride, to the calomel electrode. The tube E, fitted with a three-way stop-cock served to admit either gas or electrolyte into A as desired, while by means of the tube C and the three-way stop-cock D, connection with the air-pump could be established. The vessel was closed by means of a rubber stopper G carrying a glass tube H into which the single crystal electrode I was sealed. The under surface of the stopper was coated with a film of paraffin to prevent absorption of gas by the rubber. To render the vessel air-tight a seal of Khotinsky cement was applied between the rim of A and the stopper. The electrode vessel, salt bridge and calomel electrode were immersed in a Freas' electrically heated and controlled thermostat the water of which was maintained at 25° + 0.02°C.

All measurements of electromotive force were made by means of a Leeds and Northrup Type K potentiometer in conjunction with a suitable galvanometer and an Eppley standard cell.

Experimental Procedure

After the cell had been assembled it was placed in the thermostat and allowed to acquire the temperature of the bath. The stop-cock in the side-tube B and the stop-cock of the calomel electrode were then opened and the electromotive force of the combination was measured. Similar measurements were repeated at intervals of from fifteen to thirty minutes for a period of at least six hours. While the initial readings were found to fluctuate slightly, the readings after the first hour were quite constant and the average of the series served to establish what we shall term the "normal" potential. Having established the normal potential, a current of air was next aspirated through the electrolyte by connecting D with a jet pump and joining E with a saturator containing some of the same solution as in A. After having aspirated air through the electrolyte for twenty minutes, the stop-cocks D and F were closed and a new series of measurements was made at ten minute intervals over a period of three hours or more. The differences, ΔE, between the successive readings of the second series of measurements and the normal electromotive force were then plotted as ordinates against the time in minutes. Having determined the behavior of the electrode when immersed in the air-saturated electrolyte, the vessel A was emptied and, after thorough rinsing with fresh electrolyte, was refilled. The electrode was cleaned by dipping into a dilute solution of hydrochloric acid, washing in distilled water, drying with filter paper and then polishing with fine sand-paper. The clean electrode was replaced in A and the stopper G sealed air-tight with Khotinsky cement. The stop-cocks in B and E being closed, the vessel A and its contents were exhaused of air by means of a Hyvac pump connected at D. The exhaustion was continued until incipient ebullition was observed, when D was closed and the desired gas admitted through F. As in the case of air, measurements were made every ten minutes for the first three hours and then at less frequent intervals over an additional three or four hour period. The differences between the successive readings and the normal electromotive force were plotted against the corresponding times.

Experimental Results

It was soon found that no satisfactory duplication of results could be obtained when the experiments were repeated. While in most cases the influence of a given gas on the potential of a particular electrode in the same electrolyte was of the same order of magnitude, yet in the case of hydrogen especially, the results obtained in different experiments were found to differ markedly and in some instances quite erratically. If the variations in potential produced by circumambient gas are due to adsorption, as we are inclined to believe to be the fact, it is hardly to be expected that successive runs would yield concordant results when we reflect that the conformation of the adsorbing surface of the electrode is materially altered by the abrasion of the sandpaper in the process of cleaning after each experiment. By taking the precaution to discontinue exhaustion with the commencement of ebullition of the electrolyte and also to bubble the gases through freshly charged saturators, it was found to be unnecessary to determine the concentration of the solution remaining in A after each experiment. A series of experiments was carried out with each gas in four different concentrations of electrolyte ranging from 0.049m to 0.9870m. With each of the gases it was found that the difference between the potential of the electrode and the normal potential determined at intervals over a period of several hours was practically independent of the concentration of the electrolyte. For this reason, and because of the difficulty of satisfactorily reproducing experimental data, it is only necessary to give a series of typical curves showing the manner in which the divergence of the electrode potential from the normal varies with the time for a single concentration of electrolyte. These curves for 0.1946m $ZnCl_2$ are shown in Fig. 2 while for comparison the corresponding curves of French and Kahlenberg for zinc in normal potassium chloride are reproduced in Fig. 3. Divergences from the normal electrode potential,—represented by a heavy horizontal line,—are plotted in millivolts $\times 10^{-1}$ against the corresponding intervals of time expressed in minutes. It will be observed that the scale of ordinates in Fig. 2 is ten-fold larger than that of Fig. 3. While in general the effects produced by oxygen, nitrogen, air and hydrogen on the potential of zinc in solutions of zinc chloride have been found to bear a close resemblance to those observed by French and Kahlenberg, it is important to note that the magnitude of the effect is by no means as large. The curves of Fig. 2 show that the initial value of the potential is increased by air, nitrogen and hydrogen, whereas it is decreased by oxygen. It is also apparent that the influence of each of the gases on the potential of the metal tends to diminish with time. In proof of the statement that duplication of results was well-nigh impossible, curves plotted from the data of two different runs with both oxygen and hydrogen are shown in Fig. 2. In the case of hydrogen, while the differences between corresponding values of ΔE on the two curves vary from 0.6 to 0.2 millivolts during the first hour, much greater differences are apparent after longer intervals of time. In the experiment designated as Hydrogen (a), ΔE had become practically zero at the end of seventy minutes. This suggested that the gas had probably diffused away from the electrode and, therefore, hydrogen was again passed through the electrode vessel for another ten minutes. The gas was then turned off and measurements resumed. As indicated by the solid circles in the diagram, the value of ΔE increased about 0.7 millivolt in consequence of this second treatment with gas and then gradually fell off with time. The behavior of the electrode in the experiment designated as

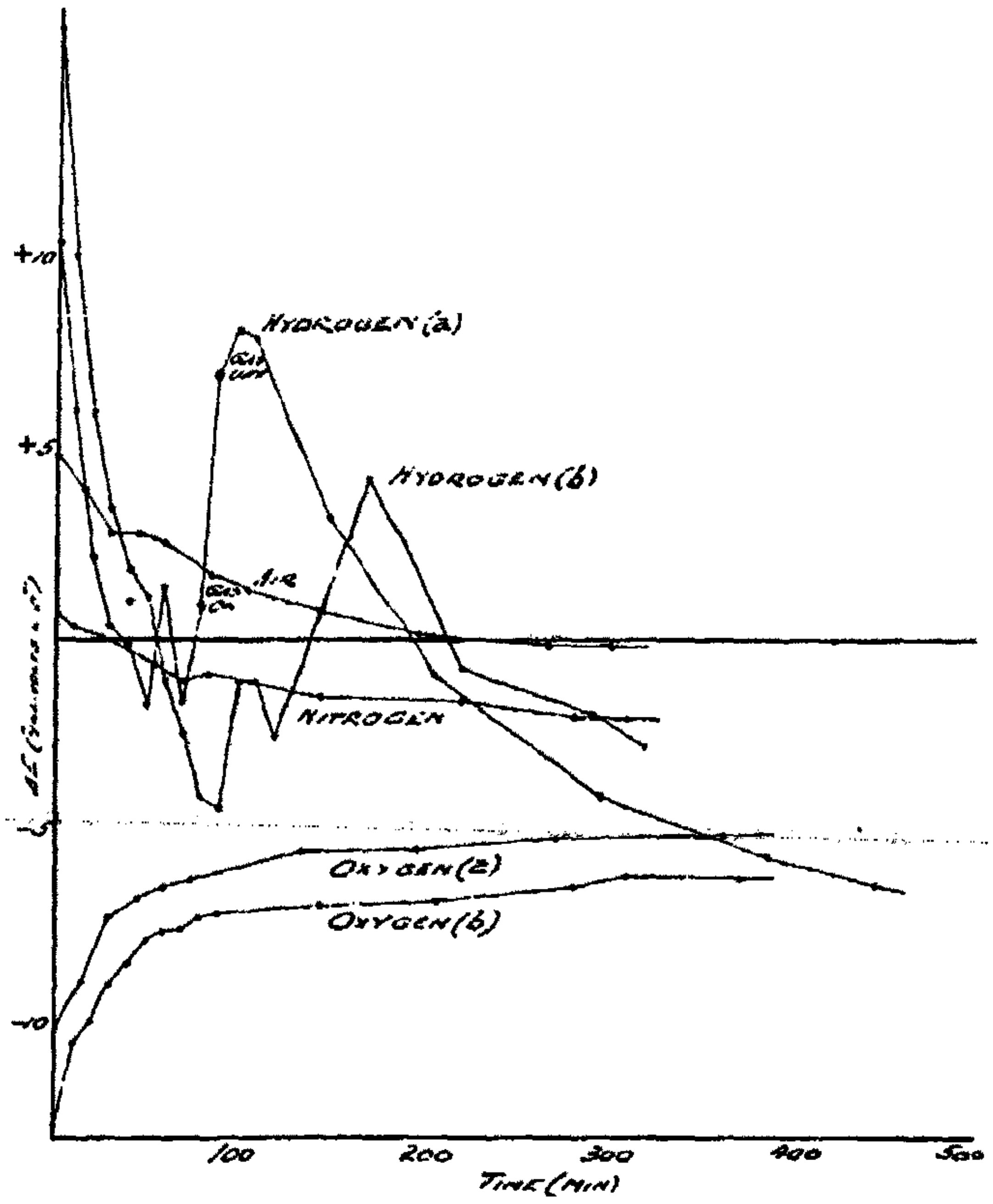

FIG. 2

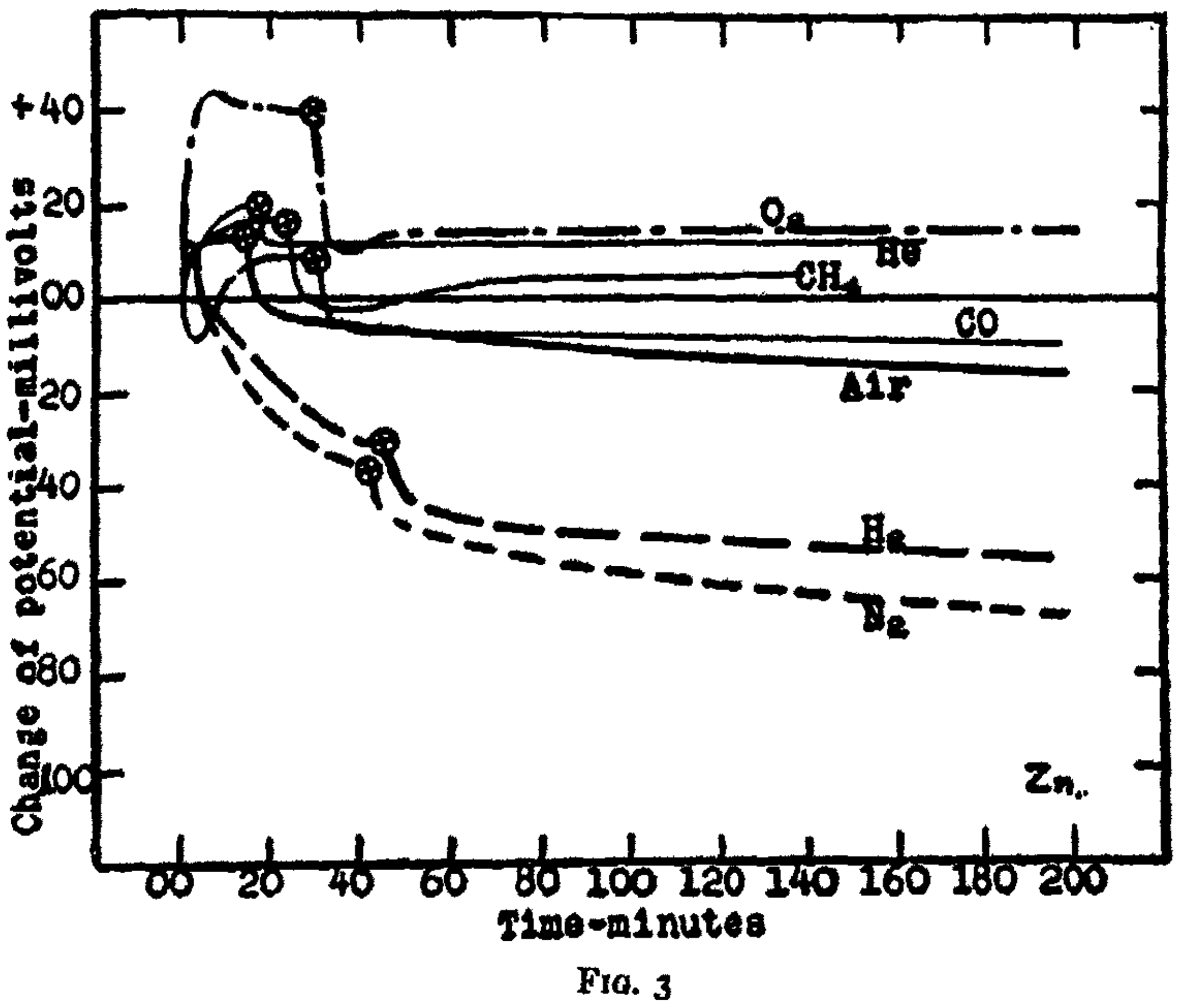

FIG. 3
⊗ Gas shut off.

Hydrogen(b), however, differs from that of the preceding experiment in that a marked increase in ΔE occurred after the first seventy minutes without any additional treatment with gas. In all of the experiments with hydrogen sudden fluctuations of electrode potential similar to those shown in Fig. 2 were observed. If fact, one is almost led to suspect the existence of some periodic phenomenon similar to those recently described by Hedges and his coworkers.[6] While the initial value of ΔE for oxygen is over 1 millivolt, it will be seen to have decreased to half-value within an interval of less than seven hours. In all of the experiments with oxygen, the curves were found to be quite free from fluctuations and their form was such as to suggest a logarithmic relation between the variables. When the logarithms of each of the two variables were plotted one against the other, the resulting graph was found to be linear, and hence the curves shown in Fig. 2 may be represented by an equation of the form

$$E = -bt^a,$$

where t denotes the time interval and where a and b are constants. On applying the equation to the experimental data from which the curves designated as Oxygen(a) and Oxygen(b) were plotted, the results given in Tables I and II were obtained.

TABLE I

$b = -15.14, \quad a = 0.1613$

t	E (calc.)	(E obs.)	Diff.
10	−10.44	−10.53	0.09
20	9.34	9.39	0.05
40	8.35	8.41	0.06
60	7.82	7.64	−0.18
80	7.46	7.18	−0.28
100	7.20	7.05	−0.15
120	6.99	6.86	−0.13
140	6.82	6.70	−0.12
160	6.68	6.58	−0.10
180	6.55	6.45	−0.10
200	6.44	6.38	−0.06
300	6.03	6.20	0.17

The close agreement between the calculated and observed values in the tables is such as to justify the conclusion that ΔE varies exponentially with the time when oxygen is present. This relation suggests that we are dealing

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[6] Hedges: J. Chem. Soc., **125**, 604 (1924); **125**, 1282 (1924); **127**, 1013 (1925); **127**, 2432 (1925); etc.

Table II

$b = -11.22$, $a = 0.1357$

t	E (calc.)	E (obs.)	Diff.
10	−8.21	8.30	0.09
20	7.47	7.50	0.03
40	6.80	6.83	0.03
60	6.44	6.45	0.01
80	6.18	6.20	0.02
100	6.01	5.95	−0.06
120	5.86	5.80	−0.06
140	5.74	5.70	−0.04
160	5.64	5.60	−0.04
180	5.55	5.56	+0.01
200	5.47	5.45	−0.02
300	5.17	5.20	+0.03

with a process of diffusion in which the initially adsorbed gas is gradually diffusing away from the electrode and thus permitting a gradual return toward the normal potential.

In reviewing the results of this investigation it would appear that when zinc is immersed in a solution of one of its salts, and hence can function as an electrode which is strictly reversible with respect to the ions of the metal, the reaction

$$Zn \rightleftarrows Zn^{++} + 2\ e,$$

takes precedence over all other reactions. Therefore, the influence of circumambient gas on the potential is much less pronounced than when the metal is immersed in a solution of some salt, such as potassium chloride, in which it cannot function reversibly.

The foregoing experiments afford confirmation of Dr. Blum's contention[4] that the potential of a metal when immersed in a solution of a salt which does not yield ions of the metal on dissociation does not afford a measure of the potential of the reversible reaction upon which the commonly accepted value of its potential is based.

While our experiments with the zinc electrode have furnished abundant proof of the fact that the presence of gases exerts some influence on the potential of the metal, the magnitude of this effect is presumably lessened by the preponderating tendency of zinc to form zinc ions in the solution of zinc chloride.

Although the exclusion of all gases from the electrolyte is a safe precaution in precise measurements of electrode potentials, the foregoing experiments indicate that the practice of displacing air by means of a current of nitrogen should cause relatively little change in potential.

Summary

1. The effect of air, oxygen, nitrogen and hydrogen on the potential of zinc immersed in solutions of zinc chloride has been studied.

2. The initial value of the potential was found to be increased by air, nitrogen and hydrogen and to be decreased by oxygen.

3. The influence of each gas on the potential of the metal diminishes with time.

4. The divergence of the potential from its "normal" value produced by oxygen falls off exponentially with time.

5. The magnitude of the change in potential produced by the different gases has been found to be much less than the corresponding change produced by the same gases when the metal is immersed in a solution of potassium chloride.

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THE THERMAL DECOMPOSITION OF ZINC AND CADMIUM CARBONATES IN AN ATMOSPHERE OF WATER VAPOR

ALEXANDER LEHRMAN AND NATHAN SPEAR

The decomposition pressures of zinc and cadmium carbonates are difficult to measure due to the slowness of reaching equilibrium. A number of attempts have been made to measure the decomposition pressure of cadmium carbonate. W. Miethke[1] tried to measure it by a static method but found great difficulty in reaching a state of equilibrium, and furthermore could not duplicate his measurements. He points out that the presence of combined water in the carbonate is necessary for the system to approach equilibrium at a measurable rate. Tzentnershver and Andrusov[2] attempted the same measurement by static and dynamic methods and claim to have succeeded. The literature does not contain the report of any measurement on the decomposition pressure of zinc carbonate.

Even though Miethke states that the presence of combined water is necessary to enable the system cadmium carbonate-cadmium oxide-carbon dioxide to reach equilibrium, the authors decided to try the effect of having an atmosphere of water vapor present. The presence of one atmosphere of water vapor also makes possible a very simple method of determining the decomposition pressure of the carbonates.

No effort was made to obtain great accuracy. The work was carried out to test the effect of the presence of an atmosphere of water vapor and to see if the simplified method was possible. In view of this it is unnecessary to take into account the small effect of one atmosphere of inert gas (water vapor) on the decomposition pressure.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1. A is the bulb in which is placed the charge of carbonate and about 10 ml. of water. The bulb is made by sealing part of a pyrex test tube to a short piece of tubing. This is connected to the manometer tube B by heavy wall rubber tubing C. The left arm of the manometer tube is about 25 cm. long and the right one is about 80 cm. long. The manometer is immersed in an open beaker (4 liters capacity) of boiling water which is kept boiling by the hot plate F. The bulb is heated by the small electric heater G. This heater was made by setting the resistance coils of a resistance furnace in a box made of asbestos board and packed with 85% magnesia. The sides of the heater were asbestos board in which holes were cut just large enough to admit the bulb on one side and the thermocouple or thermometer on the other. When inserted the bulb and thermocouple or thermometer bulb were in the center of the air space in the heater, the end of the couple or thermometer bulb being in contact with the

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[1] Dissertation, Berlin (1911).

[2] Z. physik. Chem., 123, 111 (1926); 111, 79 (1924); 115, 273 (1925).

side of the bulb holding the carbonate. The temperature within the heating box was controlled by a hand-operated rheostat and switch. The temperatures above 300° were measured with a chromel-alumel thermocouple, and below this with a mercury thermometer. The thermometer was checked against the boiling point of water. Above 300° the temperature of the heater could be kept to within 5° of the desired temperature. Near the boiling point of water the temperature could be kept to within 1° of the desired temperature.

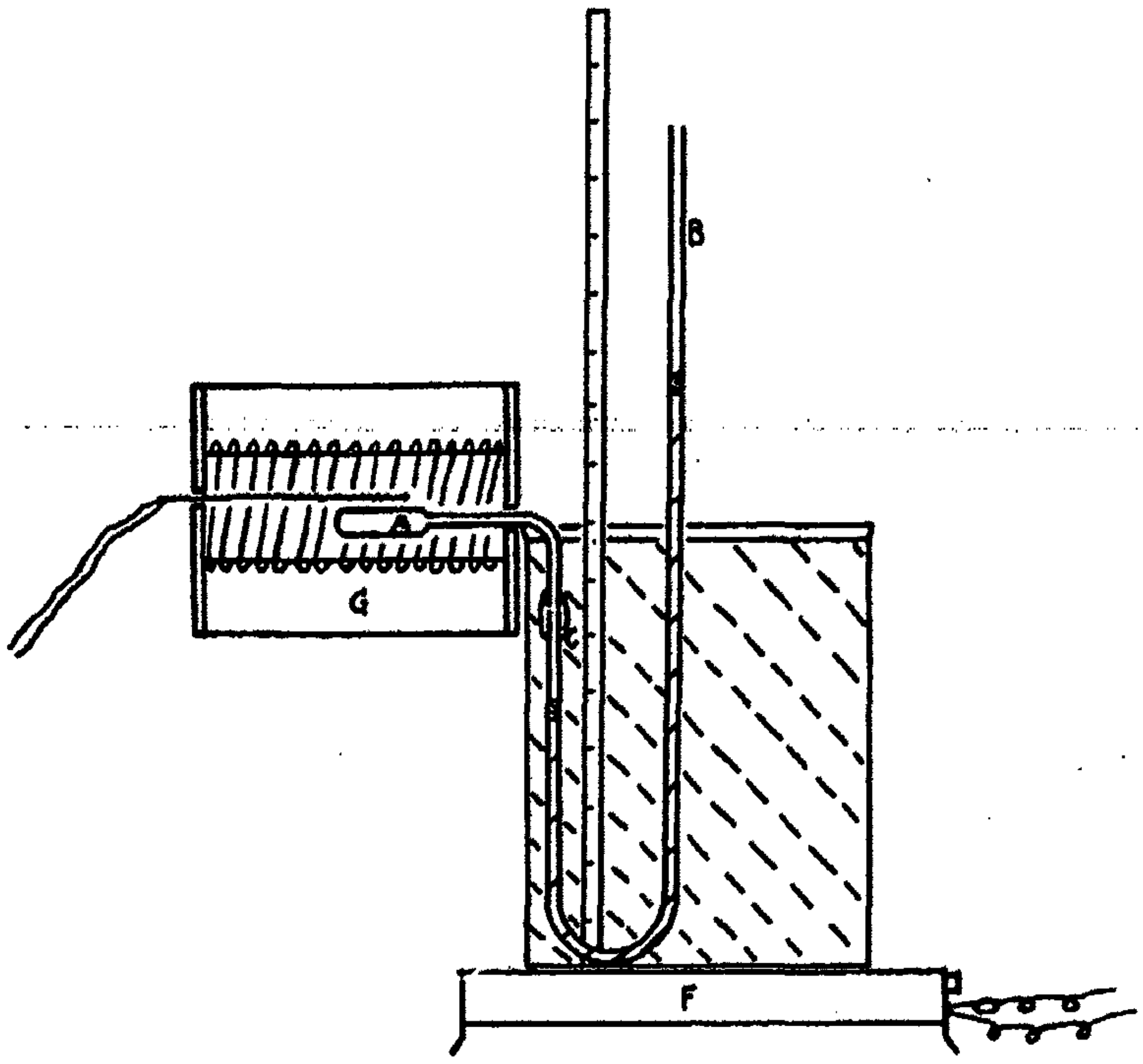

FIG. 1

The boiling water covered the short arm of the manometer tube and the tube connected to the bulb almost to the entrance to the heater. A meter stick was mounted in back of the manometer tube and the heights of mercury and water in the tubes were measured on this using a right-angle triangle to decrease errors of parallax.

Preparation of the Carbonates.—Cadmium carbonate was prepared by dissolving C. P. cadmium nitrate in water and precipitating the basic carbonate by addition of a solution of C.P. sodium carbonate. The precipitate was washed until the wash water gave no test for nitrates. It was then dissolved in concentrated ammonium hydroxide and carbon dioxide passed through until the solution was clear. The solution was then diluted with about fifty volumes of water and saturated with carbon dioxide. On standing a heavy crystalline precipitate settled out. This was washed with carbon-dioxide saturated water and then with ethanol and air-dried. That the precipitate was crystalline could be seen when it was placed under a microscope. It was analyzed by heating a weighed sample in a combustion tube and drawing dry carbon dioxide-free air over it and then through weighing bottles containing soda lime and calcium chloride. It contained water, 3.3%; carbon dioxide 24.1%; and cadmium oxide 72.6%. This indicates a molar ratio of 1 H_2O : 3.0 CO_2 : 3.1 CdO.

The method did not work so well for the preparation of zinc carbonate. The precipitate formed on dilution of the solution of the basic zinc carbonate in ammonium hydroxide with carbon dioxide saturated water had 16.8% of water, 5.2% of carbon dioxide, and 78.0% of zinc oxide. This indicates a molar ratio of 1 CO_2 : 8.3 H_2O : 8.6 ZnO.

The exact nature of the precipitates is unknown. They may be compounds, mixtures, or solid solutions. Tests, however, showed that they were free from ammonia and from nitrates. The cadmium carbonate may be the normal cadmium carbonate. Miethke[1] showed that the normal cadmium carbonate is very insoluble. This may explain why it did not hydrolyze to the extent that the zinc salt did.

Method.—2 to 3 grams of the carbonate and 10 ml. of water were placed in the bulb and the bulb connected to the manometer. The manometer tube was put into the beaker of water as shown in Fig. 1 and the water in the beaker was brought to the boiling point and kept vigorously boiling. The heater was then brought up to the bulb and the temperature raised until the water in the bulb boiled. The steam formed passed into the manometer and swept out the air. Some of the water was condensed in the manometer tube and fell to the bottom of the U. The vapor produced after this condensed in the water and the absence of air was shown by the complete condensation of the bubbles in the water. Some of the carbonate was mechanically carried over into the manometer tube, but this could in no way affect the experiment. Warm mercury was then poured into the open end of the manometer and it sank through the water forming a continuous column with some liquid water on the top of both ends of the column. As the temperature of the bulb was raised more mercury was added. The liquid water on the top of the left-side column of mercury assured a pressure of one atmosphere of water vapor in the enclosed system, and which balanced atmospheric pressure on the right hand arm of the manometer. The difference in heights of the two columns was due to the carbon dioxide pressure of the carbonate.

The pressures were read by measuring the heights of the mercury and water columns on the meter stick. The pressures due to liquid water were converted to pressures in heights of mercury by dividing by 13.6. No corrections were made for the effect of temperature on the densities of water and of mercury as the errors introduced by this are less than the experimental errors.

At the close of each determination the heater was removed and the contents of the manometer rushed back into the bulb. The apparatus was then cleaned out and made ready for the next run.

Results.—Three efforts were made to measure the decomposition pressure of cadmium carbonate in this apparatus. Equilibrium, however, could not be attained and furthermore the pressures reached under the same conditions of time and temperature in the three runs were not concordant. We can say, however, that the decomposition pressure reaches one atmosphere at about 375°, which roughly checks previous work,[1] in which the pressure of water vapor was much less than one atmosphere. The presence of water vapor seems to exert no effect on the decomposition pressure of cadmium carbonate, neither in the time taken to reach equilibrium nor on the equilibrium pressure itself.

When the zinc carbonate was put into the apparatus, however, the pressure built up very rapidly to a high value at temperatures as low as 150°. In order to work with our apparatus we had to use temperatures between 100 and 120° and a mercury thermometer was substituted for the thermocouple. Furthermore, equilibrium was rapidly reached and the reaction reversed rapidly on cooling. The results of two determinations are listed in Tables I and II. Under these conditions the carbonate had an appreciable pressure just above 100°. Table I shows that at 110° a pressure of 30 cm is reached in 5 minutes. On heating to 120° a constant pressure of about 49 cm is reached in 10 minutes. Upon cooling to 110° the pressure rapidly falls to 30 cm and on heating again to 120° approximately 49 cm pressure is again obtained. The small deviations can be explained by deviations in temperature. Table II shows that at 105° a pressure of about 20 cm is reached in 20 minutes. The fluctuations in pressure are due to variations in the temperature which was controlled only to ± 1°. On heating to 110° a pressure of 28 cm is soon attained. This checks within our experimental error the value obtained in Table I. Upon cooling to 105° the reaction immediately reverses as shown by the pressure attaining its former value.

TABLE I

Temp. °C	Pressure cm of Hg	Time minutes
110	13	0
	30	5
	31.5	10
120	36	0
	48	5
	49	10
	49.5	15
	48.5	20
	49.5	25
110	36.5	0
	37.5	5
110	31.5	10
	30	15
	29.5	20
	28.5	25
	30	30
120	40.5	0
	44.5	5
	49.5	10
	46	15
	46	25

TABLE II

Temp. °C	Pressure cm of Hg	Time minutes	Temp. °C	Pressure cm of Hg	Time minutes
105	14	0	110	27.5	10
	15	5		28	15
	13.5	10		28	20
	16	15	105	21	0
	21.5	20		19	5
	19.5	25		19	10
	19	30		20.5	15
	19	35		17	20
	21	40	110	25	0
	21	45		25	5
	21	50		25.5	10
	20	60		27	15
110	27.5	0		27	20
	27.5	5			

TABLE III

Temp. °C	Pressure cm of Hg	Time minutes	Temp. °C	Pressure cm of Hg	Time minutes
120	2	0	200	7	0
	3	30		10.5	5
	4	40		14	10
				15	15
175	5	0		16.5	20
	6.5	10		17.5	25
	7.5	20		19.5	35
	11	30		24	55
	13	40		25	65
	13.5	50			
	14	60	220	33	0
				38	10
210	23	0		52.5	20
	39.5	10		54	30
	47	20			
	50	30	200	53	0
				53	10
105	2	0		52.5	20
	1	10		52	30

For purposes of comparison a charge of zinc carbonate was put into a similar bulb and connected to a straight glass tube 90 cm long. This tube dipped into a bottle of mercury which carried a two-holed stopper. The arrangement served as a manometer. By tilting the apparatus the lower end of the tube was lifted clear of the mercury and the system evacuated through the second hole in the rubber stopper. A water aspirator was used. When the limit of evacuation was reached the apparatus was set upright and on discontinuing the action of the pump mercury rose in the tube. By comparing with a barometer the residual pressure was found to be 1.5 cm. On heating the bulb containing the carbonate, decomposition set in and the pressure of the carbon dioxide was measured by the depression of the mercury column. The results obtained are shown in Table III. It can be seen that the rate of thermal decomposition as well as the unattained decomposition pressure in the presence of only a slight pressure of water vapor is entirely different from that in an atmosphere of water vapor.

It may be that the reacting systems are different in the two cases. In the ordinary thermal decomposition the system may be represented by the components ZnO and CO_2. In the decomposition in an atmosphere of water vapor the system may be ZnO, CO_2 and H_2O, or the action may be the hydrolysis of zinc carbonate as distinguished from its decomposition.

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HYDROLYSIS OF ACETONE IN ULTRA-VIOLET LIGHT

BY M. QURESHI AND N. A. TAHIR

That an aqueous solution of acetone is hydrolysed in ultra-violet light was first pointed out by Ciamician and Silber.[1] According to the observations of these authors, when the air is not completely excluded acetic and formic acids are formed. If, however, the air is completely excluded and solutions are exposed in sealed vessels, acetic acid and methane are the products of the reaction. Henri[2] determined the quantum efficiency (γ) of the reaction and found a value of 1300. The high value of γ found in these experiments was most probably due to the evaporation of acetone from the open quartz cell employed by Henri. Later, Brown and Watts[3] using a closed cell of quartz with plane-parallel sides obtained values less than 0.2. The present investigation was undertaken with the object of determining (a) quantum efficiency of this reaction at different concentrations, (b) the influence of temperature on the quantum efficiency and the reaction-velocity, and (c) the influence of intensity on the rate of hydrolysis. The results, detailed below, have been obtained with heterogeneous ultra-violet light. Further experiments with mono-chromatic light and better methods of estimating the amount of acetic acid formed are in progress and will be reported afterwards. The discussion is postponed till the investigation is complete.

Procedure and Apparatus

A closed quartz cell with plane parallel walls was employed for exposing aqueous solutions of acetone. The amount of acetic acid formed was estimated by titrating against baryta, using phenolphthalein as indicator. A burette graduated to 0.02 cc. with a certificate of National Physical Laboratory was used for all titrations which were conducted in the light of a small electric lamp placed in a corner of the room away from the main apparatus. The usual method of preserving baryta solution in an atmosphere free from carbon dioxide and transferring it into the burette was adopted. The baryta solution was frequently standardised by means of oxalic acid. The apparatus employed was similar to the one used in a previous investigation on the photolysis of aqueous solutions of hydrogen peroxide, published in this Journal.[4] The quartz cell containing the acetone solution found itself in a small bath having quartz windows on opposite sides into which water was pumped from a thermostat placed underneath on one side. The quartz bath had a small overflow opening near the top on one side through which water flowed back to

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[1] Ber., **36**, 1582 (1903).

[2] Compt. rend., **156**, 1012 (1913).

[3] J. Chem. Soc., **129**, 1611 (1926).

[4] J. Phys Chem., **36**, 664-669 (1932).

the thermostat. The temperature of the thermostat was regulated in the usual way by means of an electric toluene regulator. In this way a continuous stream of water at a constant temperature was made to circulate through the small quartz bath. The source of light was a Quartz Mercury Lamp of the horizontal type manufactured by Hanovia Company. The lamp was placed inside a wooden box specially improvised for the purpose and lined inside with asbestos. A small electric fan placed inside behind the lamp served to ventilate the box. The ozonised air passed through an opening at the top of the box to a fume cupboard. The light of the lamp after passing through an opening in front of the box was converted into a parallel or converging beam by means of quartz lenses. A metallic reflector placed immediately behind the lamp served to increase the intensity of light. Lenses, diaphragm, quartz bath and thermopile were all mounted on an optical bench fixed permanently on a table just in front of the wooden box.

Quantum Efficiency at Different Concentrations

In these experiments acetone solutions of different concentrations were insolated in a quartz vessel with plain parallel walls, placed as described before in a small bath with quartz windows on opposite sides. The temperature of the bath was regulated at 30°C. For energy measurements a thermopile was placed immediately behind the bath and connected with a loop-galvanometer (Carl Zeiss) having an internal resistance of 6 to 10 ohms and sensitiveness of 3×10^{-7} amperes. The galvanometer was calibrated by means of a Heffner lamp both before and after the experiments. The deflections of the galvanometer were noted first with water and then with a solution of acetone in the quartz cell, the difference in the two readings corresponding to the amount of energy absorbed by the acetone solution. In calculating the number of light quanta the average wave length of the effective rays was taken as 313 mμ. After insolating acetone solutions for four hours the amount of acetic acid formed in each case was determined by carefully pipetting 5 c.cs. of the insolated solution into a small flask and titrating against baryta solution (0.012M.) The number of molecules of acetone hydrolysed per second was calculated from the amount of acetic acid formed. The ratio of this number to the number of light quanta absorbed per second gives the quantum efficiency of the reaction. The results of calculations are given below:

TABLE I

Molar concentration	Quantum efficiency γ	Molar concentration	Quantum efficiency γ
0.051	0.13	2.011	0.06
0.503	0.11	2.499	0.05
0.999	0.09	3.004	0.05
1.465	0.08	5.109	0.04

Effect of Temperature on the Quantum Efficiency

To find the effect of temperature on the quantum yield, the quantum efficiency (γ) of the reaction was determined, as previously described, at temperatures of 30°C. and 40°C. The concentration of the acetone solution was the same in each case. The following mean value of the temperature coefficient of the quantum yield was obtained from a number of determinations:

TABLE II

Temperature	Quantum efficiency	Temperature coefficient γ_{40}/γ_{30}
30°C.	0.12	1.41
40°C.	0.17	

Temperature Coefficient of the Reaction Velocity

To find the effect of temperature on the reaction velocity, acetone solutions of equal strength were insolated at temperatures of 30°C. and 40°C. in quartz vessels with plane parallel walls. The amount of acetic acid formed in each case was determined by titrating against the standard baryta solution (0.013 N.). Experimental conditions were the same in the two sets of experiments. The average results of a number of experiments are given below:

TABLE III

Concentration of the Solution = 0.044M

Temperature	Time of insolation	Amount of acetic acid in c.cs. of baryta solution	Temperature coefficient k_{40}/k_{30}
30°C.	4 hours	0.085	1.52
40°C.	4 hours	0.130	

Effect of Intensity

The effect of intensity on the rate of hydrolysis of acetone was determined by two different methods. In the first set of experiments the intensity was varied by means of a rotating sector placed between the reaction vessel and the source of light. In the second set of experiments the aperture of the diaphragm was changed to vary the intensity. The amount of acetic acid formed in 4 hours with different sector openings and with different apertures of the diaphragm was determined by titrating against standard baryta solution. Temperature was kept constant at 30°C.

The results of these experiments are given in Tables IV and V.

TABLE IV

Method: Rotating Sector
Velocity of Rotation = 500 revolutions per minute
Concentration = 1.439M.
Temperature – 30°C.

Sector angle	Relative intensity	Amount of acetic acid formed in c.cs. of baryta solution	Rate of change / Intensity
360°	4	0.12	0.03
180°	2	0.07	0.035
90°	1	0.03	0.03

TABLE V

Method: Variation of diaphragm opening.
Concentration = 1.439M.
Temperature = 30°C.

Relative intensity	Amount of acetic acid formed in c.cs. of baryta solution	Rate of change / Intensity
9	0.25	0.028
4	0.14	0.035
1	0.03	0.03

Summary

1. The quantum efficiency of the hydrolysis of acetone in ultra-violet light was determined at different concentrations (0.05M–05M). Its value varies between 0.13 and 0.14.

2. The quantum efficiency was determined at two different temperatures viz. 30°C. and 40°C. The ratio of its values at these temperatures, i.e. the temperature coefficient of the quantum yield, is 1.41.

3. The temperature coefficient of the reaction velocity (k_{40}/k_{30}) is found equal to 1.52.

4. The influence of intensity on the rate of hydrolysis of acetone in ultra-violet light was determined by the methods of rotating sector and variation in the diaphragm opening. The results in both cases show that the rate of hydrolysis is directly proportional to the intensity.

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May 31, 1932.

THE THEORY OF THE ADSORPTION OF GASES ON SOLIDS

BY R. S. BRADLEY

Adsorption is a very complicated process. It may be activated, or the energy of activation may be negligible, and the type of activation may change with the temperature. Lateral mobility of the adsorbed molecules, diffusion into the interior either through the lattice or more probably along crystallite boundaries, vibration perpendicular and parallel to the surface, collisions between adsorbed molecules and those striking the surface, or between adsorbed molecules on the surface, the rotation and dissociation of adsorbed molecules, may all have to be considered.[1] In this paper certain aspects of adsorption which have to do with the relation between the surface and bulk phases will be studied.

I. The Application of the 'Morse curve' to Adsorption

Frenkel[2] considered the potential energy of an adsorbed molecule to be of the form $-u_0 + \Delta u$, where Δu is given by the simple harmonic formula $2\pi^2/\tau_0^2 \, . \, mz^2$: τ_0 is the period of oscillation perpendicular to the surface, m is the mass of the adsorbed molecule, and z is its distance from the equilibrium position. Instead of this parabolic curve it will certainly be closer to reality to use a potential energy curve of the form shown (Fig. 1). A good approximation to this type of curve was given by Morse[3] in the form

$E(r) = u_0 e^{-2a(r-r_0)} - 2u_0 e^{-a(r-r_0)}$, where a is a constant connected with τ_0 by the relation $\frac{1}{\tau_0} = \frac{a}{2\pi}\left(\frac{2\,u_0}{m}\right)^{\frac{1}{2}}$, if the surface is regarded as a massive body at rest on which the adsorbed molecule oscillates. Hence $\Delta u = u_0 e^{-2az} - 2\,u_0 e^{-az} + u_0$, where $z = r - r_0$.

Frenkel calculated the thickness of the adsorption phase, δ, from the relation

$$\delta = \int_{-\infty}^{\infty} e^{-\Delta u/kT}\, dz = \tau_0 \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}.$$

Then, applying $n/S = c_0\, \delta\, e^{u_0/kT}$, $n = \nu\tau$,

$$\nu = S\, c_0 \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$$

(where n molecules are adsorbed on an area S, c_0 is the bulk concentration, and τ is the mean life of an adsorbed molecule: ν is the number of molecules striking an area S per second), we obtain

$$\tau = \tau_0 e^{u_0/kT}$$

On the basis of a 'Morse curve' this calculation becomes

$$\delta = \int_{-r_o}^{\infty} e^{-\Delta u/kT}\, dz = \frac{1}{a}\int_{o}^{\infty} \frac{e^{-c^2(u-1)^2}}{u}\, du,$$

where $u = e^{-az}$, e^{ar_o} is equal to ∞, and $c^2 = u_o/kT$.

This integral may be split up into two parts, $\int_1^{\infty}$ and $\int_o^{1}$. To evaluate

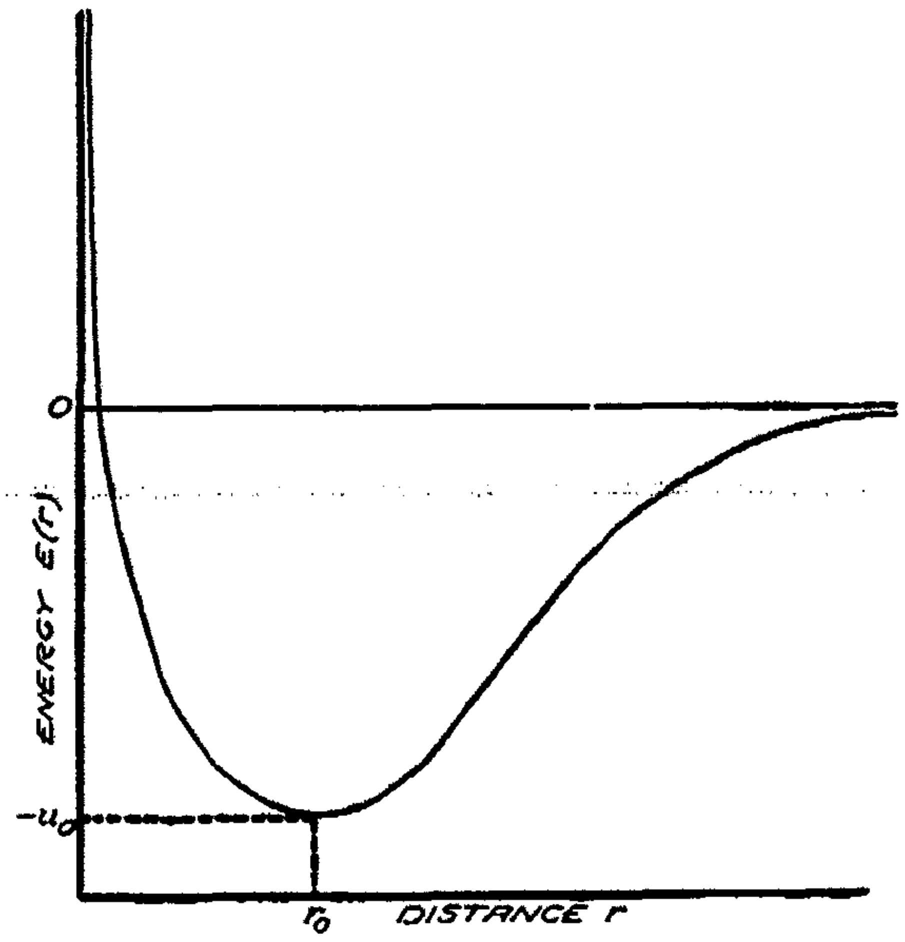

Fig. 1

the first part put $c(u - 1) = w$. This gives

$$\frac{1}{a}\int_{1}^{\infty} \frac{e^{-c^2(c-1)^2}\, du}{u} = \frac{1}{a}\int_{o}^{\infty} \frac{e^{-w^2}\, dw}{w+c} \qquad 1$$

$$\text{Now} \int_{o}^{\infty} \frac{e^{-w^2}\, dw}{(w+c)^2} = -\left[\frac{e^{-w^2}}{w+c}\right]_o^{\infty} - \int_{o}^{\infty} \frac{2w}{w+c} e^{-w^2}\, dw$$

$$= \frac{1}{c} - 2\int_{o}^{\infty} e^{-w^2}\, dw + 2c\int_{o}^{\infty} \frac{e^{-w^2}}{w+c}\, dw$$

In practice c will be usually 4 or greater, corresponding to $u_o = 10{,}000$ cals at room temperatures (even when u_o is only 2500 cals c is 2). Hence we may approximate to the value of $\int_o^{\infty} \frac{e^{-w^2}\, dw}{(w + c)^2}$ by putting $w = o$, giving

$$\frac{\sqrt{\pi}}{2c^2} = \frac{1}{c} - \sqrt{\pi} + 2\, c\int_{o}^{\infty} \frac{e^{-w^2}}{w+c}\, dw$$

Hence the value of the first part is $1/a \,.\, (\sqrt{\pi}/2c - 1/2c^2 + \,..)$ app. 2

The second part is $\frac{1}{a}\int_0^1 \frac{e^{-c^2(1-u)^2}}{u}\,du = \frac{1}{a}\int_{-c}^{0} \frac{e^{-w^2}}{w+c}\,dw$

$$> \frac{1}{a}\int_{-c}^{0} \frac{e^{-c^2}}{w+c}\,dw > \frac{1}{a}e^{-c^2}\,[\log(w+c)]_{-c}^{0} = \infty.$$

The method of Frenkel, therefore, does not give a finite result when applied to the more correct model. This difficulty may be removed by calculating the quantity adsorbed from the bulk gas, or the surface excess. If the number of molecules per cm^3 at the plane z is n_z we may write

$$n_z = c_0\, e^{u_0(-\Delta u/kT)} = c_0 \,.\, e^{u_0/kT} \,.\, e^{-\Delta u/kT} \qquad 3$$

neglecting the size of the molecules. Hence the quantity adsorbed is given by

$$S\, c_0\, e^{u_0/kT}\int_{-r_0}^{\infty}(e^{-u\Delta/kT} - 1)\,dz = \frac{S\, c_0}{a}\, e^{u_0/kT}\int_{-c}^{\infty}\left(\frac{e^{-w^2} - e^{-c^2}}{w+c}\right)dw$$

The last integral is now finite when $w = -c$, for on putting $w = -c + \epsilon$,

$$\frac{e^{-w^2} - e^{-c^2}}{w+c} = e^{-c^2}\left(\frac{e^{-\epsilon^2+2\epsilon c} - 1}{\epsilon}\right) = \frac{e^{-c^2}}{\epsilon}(\epsilon^2 + 2c\epsilon \ldots) = 2ce^{-c^2} \text{ when } \epsilon \to 0.$$

As before $\int_{-c}^{\infty}\frac{e^{-w^2} - e^{-c^2}}{w+c}\,dw$ may be split up into two parts.

a) $\int_0^{\infty}\frac{e^{-w^2}\,dw}{w+c}$ has been calculated. $\int_0^{\infty}\frac{e^{-c^2}}{w+c}\,dw = \int_{-r_0}^{0} e^{-c^2}\,dz = e^{-c^2}\,r_0$, and is negligible.

b) $\int_{-c}^{0}\frac{e^{-w^2} - e^{-c^2}}{w+c}\,dw = I$. When c is of the order 4 it will be sufficiently accurate to take $I = \int_{-c/2}^{0}\frac{e^{-w^2}}{w+c}\,dw$, since the contribution of the term e^{-c^2} is small in this range, and since the value of the integral in the range $-c/2$ to $-c$ is small compared with the portion in the range $-c/2$ to 0.

$$\text{Now } \int_0^{-c/2}\frac{e^{-w^2}}{(w+c)^2}\,dw = \left[-\frac{e^{-w^2}}{w+c}\right]_0^{-c/2} - 2\int_0^{-c/2} e^{-w^2}\,dw + 2c\int_0^{-c/2}\frac{e^{-w^2}}{w+c}\,dw.$$

Hence, as before, $I = \sqrt{\pi}/2c - 1/2c^2$. The quantity adsorbed is therefore

$$n = \frac{S\, c_0}{a} \cdot e^{u_0/kT}\left(\frac{\sqrt{\pi}}{c} - \frac{1}{c^2}\right)$$

On inserting the value of a · , and on putting $n/\tau = \nu$ we get

$$\tau = \tau_0 \left(1 - \sqrt{\frac{kT}{\pi u_0}} \right) e^{u_0/kT}$$

as the modified Frenkel relationship. It will be noticed that the correction is small, but that Frenkel's definition of δ should run $\delta = \int_{-\infty}^{\infty} (e^{-\Delta u/kT} - 1)\, dz$. This definition will not give a finite value for δ when the potential energy curve is parabolic, and only by combination of inexact definitions of δ and of the potential energy curve can a finite result be obtained by Frenkel's method.

II. The Unimolecular Film

In the above treatment, using the Morse curve, τ_0 appears merely as a constant in the potential energy curve, and no reference is made to the actual oscillations of the adsorbed molecules. Equation 3 gives a gradually increasing concentration up to the minimum in the potential energy curve. In actual practice the bulk of the adsorbed film will probably be confined to a unimolecular layer, not necessarily closely packed, and secondary adsorption, if it occurs (as for example with water), will be weaker. It is also desirable for simplicity to regard the adsorption as unimolecular, for a molecule in the second layer will not have the same potential energy curve as one in the first.

At first sight there seems little connection between this point of view and the one in which the concentration is supposed to vary continuously up to the surface. But any given molecule of the unimolecular film will be oscillating, and will spend most of its time at the extreme positions of its oscillations. As an approximation suppose it spends all its time there. Then we again get a "static' spatial distribution. If there are n_0 mols. per cm.^{3} at the equilibrium position the number at the plane z is $n_0\, e^{-\Delta u/kT}$ and at the plane ∞ $n_0\, e = {}^{-u_0/kT} = c_0$, where c_0 is the bulk concentration. Hence as before

$$n = S \int_{-r_0}^{\infty} (n_0\, e^{-\Delta u/kT} - c_0)\, dz = S\, c_0 \int_{-r_0}^{\infty} (e^{-E_z/kT} - 1)\, dz$$

Owing therefore to oscillation the unimolecular film gives a volume distribution as before. This spatial unimolecular layer is really what is considered in section I, since a molecule in the second layer as ordinarily defined will not have the same oscillation constants as one in the first layer.

III. Correction for the Finite Size of the Adsorbed Molecules

When part of the available space is excluded because of the finite size of the molecules equation 3 can no longer be applied. This correction is important, because the concentration near the surface is high.

Let v_0 be the volume of a molecule. Then equation 3 could be replaced by

$$\frac{n_z}{1 - n_z\, v_0} = \frac{c_0\, e}{1 - c_0\, v_0}^{-E_z/kT} = c_0\, e^{-E_z/kT}, \text{ since } c_0\, v_0 \ll 1.$$

This equation gives $n_z = 1/v_0$ when E_z is very large, as it should, for then close packing will occur.

Hence

$$n = S\int_{-r_0}^{\infty}(n_z - c_0)\,dz$$

$$= S\int_{-r_0}^{\infty}\left(\frac{c_0\,e^{-E_z/kT}}{1+c_0\,v_0\,e^{-E_z/kT}} - c_0\right)\cdot dz$$

This equation cannot be integrated as it stands, although a graphical evaluation is of course possible when E_z is known. An approximation can however be obtained as follows.

$$n = S\,c_0\,e^{u_0/kT}\int_{-r_0}^{\infty}\left(\frac{e^{-\Delta u/kT}}{1 + c_0\,v_0\,e^{-E_z/kT}} - e^{-u_0/kT}\right)dz$$

$$= S\,c_0\,e^{u_0/kT}\int_{-r_0}^{\infty}(1-n_z\,v_0)\,(e^{-\Delta u/kT} - e^{-u_0/kT})\,dz$$

Now replace $1-n_z\,v_0$ by its mean value between the limits $-d/2$ and $d/2$, where d is the molecular diameter. The major portion of the integral will fall in these limits

$$\therefore \qquad \int_{-d/2}^{d/2} n_z\,dz = n/S \text{ app.}$$

$\therefore$ mean value of $n_z = n/dS$

and mean value of $1 - n_z\,v_0 = 1 - \dfrac{nv_0}{Sd} = \dfrac{S - n\sigma_0}{S}$

where σ_0 is the area on the surface appropriated by one molecule and into which another cannot enter.

$$\text{Hence } \frac{n}{S - n\sigma_0} = c_0\,e^{u_0/kT}\int_{-r_0}^{\infty}(e^{-\Delta u/kT} - e^{-u_0/kT})\,dz$$

$$= \frac{c_0}{a}e^{u_0/kT}\left(\frac{\sqrt{\pi}}{c} - \frac{1}{c^2}\right)$$

$$= \frac{c_0}{a}e^{u_0/kT}\,\frac{\sqrt{\pi}}{c}\left(1 - \sqrt{\frac{Tk}{\pi u_0}}\right)$$

This is, in fact, the form of Langmuir's isotherm, and we see that this form is determined by the allowance for the finite volume of the molecules.

IV. The Mean Life of Adsorbed Molecules and the Adsorption Isotherm

It follows therefore that Frenkel's deduction of the mean life of an adsorbed molecule must be revised, for in that deduction proportionality was taken between quantity adsorbed and the pressure. Before this is done, however, another correction to Frenkel's calculation must also be applied, namely, an allowance for the reflexion coefficient.

Let a fraction e be reflected from the surface. Then

$$n/\tau = (1 - e)\ \nu$$

e is dependent on the surface concentration. For suppose a molecule from the gas on hitting an adsorbed molecule is either reflected (fraction x), or is reflected with the adsorbed molecule, which has been activated for desorption by collision (fraction y): finally a fraction z may be adsorbed by displacing to the side the molecule on the surface with which the gas molecule collides. Then $x + y + z = 1$. On the other hand suppose that a molecule on hitting a free space is adsorbed with probability β.[4]

$$\text{Then } e = n\sigma_0/S\,.\,(x + 2y - z) + (1 - \beta)\,(1 - n\sigma_0/S)$$

$$= n\sigma_0/S\,.\,(1 + y - 2z) + (1 - \beta)\,(1 - n\sigma_0/S)$$

$$\text{Hence } (1 - e) = \beta - n\sigma_0/S\,.\,(y + \beta - 2z).$$

When, therefore, the surface is closely crowded, $1 - e = 2z - y$. Normally, however, $y - 2z$ may be neglected compared with β, and hence

$$(1 - e) = \beta\,(1 - n\sigma/_0S) \text{ and } n/\tau = \beta\nu/S\,.\,(S - n\sigma_0) \qquad 4$$

On combining this result with the equations

$$\frac{n}{S - n\sigma_0} = c_0\,\frac{\cdot}{a}\,e^{u_0/kT}\,\frac{\sqrt{\pi}}{c}\text{ app.}$$

$$\frac{1}{\tau_0} = \frac{a}{2\pi}\left(\frac{2\,u_0}{m}\right)^{\frac{1}{2}}$$

$$\nu = S\,c_0\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}$$

we get $\beta\tau = \tau_0\,e^{u_0/kT}$ 5

Now from 4 $$n = \frac{\beta\nu\tau S}{S + \sigma_0\beta\nu\tau}\text{ (Langmuir's isotherm)}$$

Hence $$\frac{n}{S} = \frac{\tau_0\,e^{u_0/kT}\,p/(2\pi mkT)^{\frac{1}{2}}}{1 + \tau_0\,\sigma_0\,e^{u_0/kT}\,p/(2\pi mkT)^{\frac{1}{2}}}$$

where p is the bulk pressure. This is the equation Frenkel deduced, although he obtained it by neglecting β, and by inserting in Langmuir's equation (in which n is not proportional to the pressure) the result $\tau = \tau_0\,e^{u_0/kT}$ deduced on the assumption of proportionality between n and the pressure.

On writing the isotherm in the usual form $\frac{n}{S} = \frac{c_1c_2p}{1 + c_2\,p}$

we have $$c_1\,c_2 = \frac{\tau_0\,e^{u_0/kT}}{(2\pi mkT)} \qquad 6$$

$$c_1 = 1/\sigma_0 \qquad 7$$

The form 6 was deduced by Bradley[5] from general thermodynamic reasoning, neglecting the small effect of the power of T in the temperature coefficient, and shown to agree with experiment. Little can be said on the variation of c_1 with temperature given by equation 7.

V. The Formation of Agglomerates on the Surface

Frenkel explained the existence of a critical temperature for the condensation of atomic beams by the formation of pairs of combined atoms on the surface. When an allowance is made for the reflection coefficient the deduction for the critical stream density must be modified. For then

$$dn/dt = \nu\,(1 - e) = w_1n_1 - w_2n_2$$

where there are n_1 and n_2 single and double molecules on the surface of mean lives $1/w_1$ and $1/w_2$. Hence at equilibrium $\nu\beta(1 - n\sigma^{\circ}/S) - w_1n_1 - w_2n_2 = 0$

$$\nu\beta(1 - n\sigma_o/S) - w_1(n - n^2\sigma/S) - w_2\,n^2\sigma/S = 0, \text{ where } \sigma = \sigma_o\,e^{E_o/kT},$$

and E_o is the dissociation energy of the doublet $(\sigma > \sigma_o)$.

Hence $\frac{n^2\sigma}{S}(w_1 - w_2) - n\left(w_1 + \frac{\nu\beta\sigma_o}{S}\right) + \nu\beta = 0$, and n is real only if

$$\left(w_1 + \frac{\nu\beta\sigma_o}{S}\right)^2 > 4\,\frac{\beta\sigma}{S}\,(w_1 - w_2)\nu > 4\nu\beta\beta' \text{ where } \beta' = \frac{\sigma}{S}\,(w_1 - w_2)$$

The critical value of ν is given by $\frac{\nu^2\beta^2\sigma^2}{S^2} + \nu\left(\frac{2w_1\beta\sigma_o}{S} - 4\beta\beta'\right) + w_1^2 = 0$,

or $$\nu = \left[4\,\beta\beta' - 2\,\frac{w_1\beta\sigma_o}{S} \pm 4\,\sqrt{\beta^2\beta'^2 - \frac{w_1\beta^2\beta'\sigma_o}{S}}\right]\frac{S^2}{2\beta^2\sigma^2}$$

in place of Frenkel's relation $\nu = \frac{w_1^2}{4(w_1 - w_2)}\,\frac{S}{\sigma}$

The term under the root is $\beta^2\beta'^2\left(1 - \frac{w_1\sigma_o}{\beta' S}\right)$, and if $w_1 - w_2$ is of the same order as w_1, $\frac{w_1\sigma_o}{\beta' S}$ is small.

Hence $$\frac{2\beta^2\sigma^2\nu}{S^2} = 4\beta\beta' - 2\,\frac{w_1\beta\sigma_o}{S} \pm \left(4\,\beta\beta' - 2\,\frac{\beta w_1\sigma_o}{S} - \frac{w_1^2\beta\sigma_o^2}{2\beta' S^2}\;\ldots\ldots\right)$$

and $\nu = 4\sigma(w_1 - w_2)\,\frac{S}{\sigma_o^2\beta}$ or $\frac{w_1^2\,S}{4\beta\sigma(w_1 - w_2)}$.

When, therefore $\nu > \frac{w_1^2 S}{4\beta\sigma(w_1 - w_2)}$ and $< 4\,\frac{\sigma}{\sigma_o^2\beta}\,(w_1 - w_2)S$ the value of $\frac{\nu^2\beta^2\sigma^2_o}{S^2} + \nu\left(\frac{2w_1\beta\sigma_o}{S} - 4\beta\beta'\right) + w_1^2$ is negative, and n is not real. No equilibrium exists between these limits. There are two critical points instead of one.

This result is still obtained if the theory is elaborated in terms of potential energy curves between pairs of molecules on the surface. Let the energy curve between two molecules be E(r), where r is measured along the surface. Select one molecule. Then the chance that the centre of a second molecule is between r and r + dr of the centre of the first is $\frac{2\pi r\,.\,dr}{S}$. This assumes that all parts of the surface are equally accessible to the second molecule, and that the first molecule is not on the edge of S.

Since there are n molecules on S the chance that any one of these has its centre between r and r + dr of that of the selected molecule is $\frac{2\pi r.dr}{S}\frac{1}{2}n(n-1)$, since each pair will be counted twice. Owing to the intermolecular force this will become $\frac{\pi r.dr}{S}\,n\,(n-1)\,e^{-E(r)/kT}$.

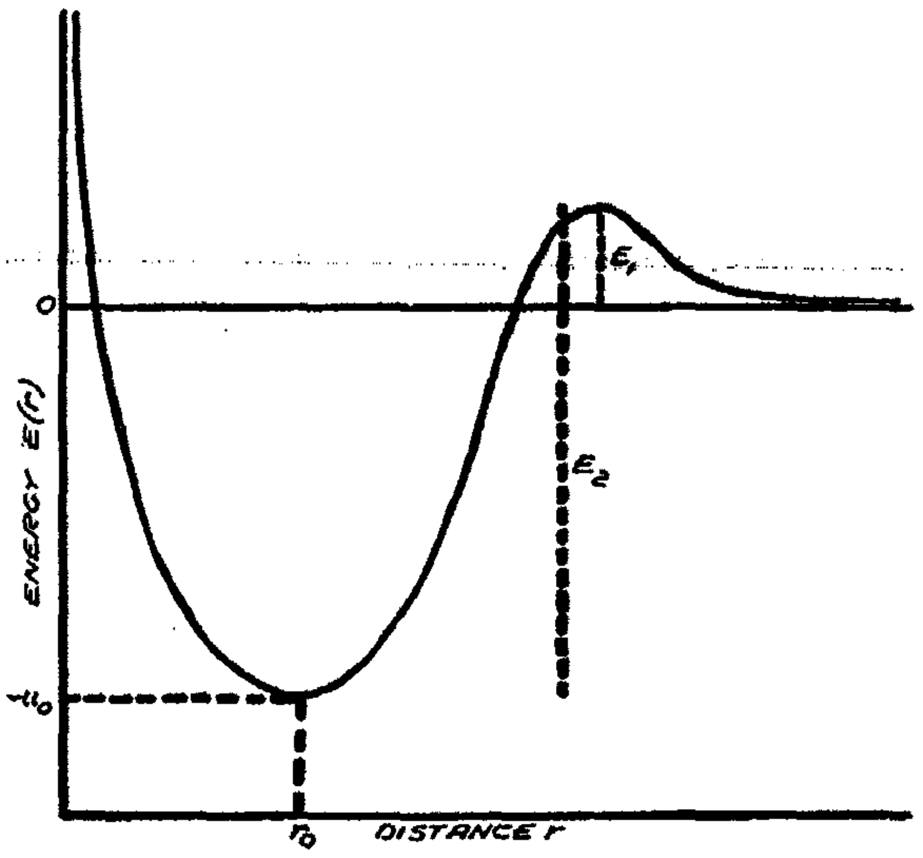

Fig. 2

Theoretically the influence of one molecule on another extends to great distances. Actually, however, at distances greater than some value d_1 the effect of one molecule on another will be negligible. Those pairs with centres less than d_1 apart may be regarded as a double molecule.

$$\text{Hence}\ \frac{dn}{dt} = \nu(1-e) - w_1\left(n - \int_0^{d_1}\frac{\pi n^2}{S}e^{-E(r)/kT}.r.dr\right) - \int^{J_1}\frac{n^2\pi}{S}e^{-E(r)/kT}rw_r\,dr$$

where w_r is the value of $1/\tau_r$, and τ_r is the mean life of a molecule in a pair with centres a distance r apart. The last equation is of the form

$$\frac{dn}{dt} = \beta\nu\left(1 - \frac{n\sigma_o}{S}\right) - w_1\,[n - n^2\,\Phi\,(d_1)] - n^2\,\Omega\,(d_1),$$

of the same type as before.

VII. Activated Adsorption

It may happen that β corresponds to an activated adsorption,[6] only a fraction $e^{-E_1/kT}$ of the impinging molecules entering the adsorption phase. Then the relation $\beta\tau = \tau_0 e^{u_0/kT}$ becomes $\tau = \tau_0 e^{E_1/kT}$, (instead of $\tau = \tau_0 e^{u_0/kT}$), where E_2 is the activation energy required for desorption. This gives a form for the rate of desorption which is independent of the reverse reaction. E_1 can be accounted for by a potential energy curve of the type shown (Fig. 2). The calculation of δ will not be affected by the small rising of the curve above the zero axis, as the contribution to the integral of this portion is small. However the rate of desorption will be affected. The adsorbed molecules will have various amplitudes, corresponding to various energy levels, and strictly they will be anharmonic oscillators, the frequency varying with the amplitude. For simplicity suppose that they all have the same frequency $1/\tau_0$. Any particular molecule will leave the surface when its energy, kinetic and potential, exceeds the energy at the lowest point of the potential energy curve by E_2, taking this lowest point as the zero reference point for the energy. A molecule has a chance to evaporate $1/\tau_0$ times per second, and if all the molecules were activated the rate of evaporation would be n/τ_0 per area S. Only a fraction $e^{-E_2/kT}$ is activated, however, and supposing that the supply of active molecules can be maintained the rate of evaporation will be $n/\tau_0 e^{-E_2/kT} = n/\tau$, giving the required relation. It is interesting to notice that Alty's[7] results on the evaporation of water can be interpreted by writing his absorption coefficients in the form $e^{-E_1/kT}$ where E_1 is about 2600 cals.

If desorption resembles the dissociation of a molecule in this way there is the interesting possibility that the activation may be effected by means of a light quantum.

My thanks are due to Mr. Gilham for mathematical advice.

References

[1] See Trans. Faraday Soc., **28**, Parts 3 and 4 (1932).

[2] Frenkel: Z. Physik, **26**, 117 (1924).

[3] Morse: Phys. Rev., (2) **34**, 57 (1929).

[4] See also Clausing: Ann. Physik, [5] **7**, 489, 522 (1930).

[5] Bradley: Phil. Mag., **11**, 690 (1931). The equation of page 695 should run $1/c_1 = .05073 - 16.26/T + 3.10^5/T^3$, giving a constant value to c_1 at high temperatures as stated.

[6] Taylor: Trans. Faraday Soc., **1932**, Parts 3 and 4.

[7] Alty: Proc. Roy. Soc., **131A**, 554 (1931).

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June 16, 1932.

NEW BOOKS

An Introduction to the Principles of Physical Chemistry. *By O. Maass and E. W. R. Steacie. 24 × 16 cm; pp. vii + 277. New York and London: John Wiley and Sons, Chapman and Hall, 1931. Price: $2.75.* "This book is intended to be used as a first course in physical chemistry for students who have had elementary courses in chemistry, physics, and mathematics. A course of about 50 lectures has been given at McGill University for the past 12 years in this form to a class composed of those intending to make chemistry their profession, chemical engineers, and students intending to enter medicine and the biological sciences. These students have either not had calculus, or are taking courses in it concurrently with physical chemistry. In the case of students intending to specialize in chemistry it has been found advisable to bring in an elementary course such as this at the earliest possible stage in their training. This makes possible a better appreciation of more advanced and detailed courses in physical chemistry, since the student thus has several years in which to assimilate the fundamental ideas," p. v.

The chapters are entitled: introduction; the structure of matter; the gaseous state of aggregation; the transition from the gaseous to the liquid state; the liquid state of aggregation; the solid state of aggregation; energy and the structure of matter; mixtures, solutions, and compounds; solutions; the theory of solutions; chemical equilibria; the velocity of chemical reactions; electrolytic dissociation; applications of the ionic hypothesis; thermochemistry.

As emphasized in the preface the authors believe in giving an introductory and a more advanced course in physical chemistry. One justification for this is given on p. 2. "Today specialization in a fairly narrow field is necessary. Although this is true, it is nevertheless essential that phenomena which apparently differ widely should be correlated as much as possible. Hence, in order to pursue one branch of science successfully, it is necessary to have a working knowledge of all related subjects."

Another justification is given on p. 10. "Among the prerequisites for a comprehensive study of physical chemistry mathematics takes an important place. It does so from two rather different points of view. Of these, the ability to utilize mathematical manipulations in specific problems in physical chemistry is perhaps of less importance than the training in exact thinking and in certain logical systems of reasoning. Except in a few minor divisions of physical chemistry the mathematical technique required is of the simplest kind, involving only the elementary principles of calculus and analytical geometry. For an elementary introduction to the subject, such as this book, even these are not required to any great extent."

The reviewer believes that the authors are right in their point of view and that chemists should be given a general knowledge of physical chemistry with as little mathematics as possible. After that the mathematically inclined can follow their natural bent. On p. 172 the authors say that "solution is thus completely analogous to evaporation." They are thinking unconsciously in terms of mathematics. The reviewer would like to see the further statement that "solution is thus completely analogous to melting. A solution is a mixture of liquids. The gas laws are applicable to some extent to the components."

"In the case of water, the data indicate that the molecules in the liquid state are partly $(H_2O)_2$ and partly $(H_2O)_3$. These are referred to as dihydrol and trihydrol, respectively. In the case of the latter, for example, there are 9 atoms in the molecule. These move about as a separate and distinct unit. None of them can be displaced without the displacement of the remainder in such a way as to preserve their relative positions. Liquid water is thus a mixture of different molecules, and all we can do is to assign to it an average molecular weight," p. 106.

"The second law [of thermodynamics] is based on experimentally observable systems, in which the average velocity of a large number of molecules is under consideration. The second law is only a statistical truth, which holds when the number of molecules concerned is large. That Maxwell's suggested mechanism is actually observable experimentally will be made evident later in connection with the Brownian movement of colloidal particles," p. 119.

On the assumption that the hydrogen ion is not hydrated, the authors give the following values, p. 221, for some other ions: K, 20; Ag, 35; Cu, 55; Na, 70; Li, 150; OH, 10; Cl, 20; NO_3, 25. It is undoubtedly perfectly safe to believe that these values are not right.

Wilder D. Bancroft

Smoke: A Study of Aerial Disperse Systems. *By R. Whytlaw-Gray and H. S. Patterson. Pp. viii + 192. London: Edward Arnold and Company, 1932. Price: 14 shillings.* The study of those disperse systems in which a liquid or solid substance is dispersed in a very finely divided condition in a gas or vapour is of peculiar interest to the physical chemist. It leads to such interesting problems as the precise mechanism of smoke formation by the condensation—under many guises—of a diluted vapour, the manner of growth of the freshly formed particles, the extent to which the subsequent behaviour of the particles is affected by the adsorption of gas molecules or ions, the possibility of the smoke particles exerting a catalytic action upon a reaction between two or more constituents of the dispersion medium, and the mechanism by which the smoke particles themselves may react directly with some constituent of the gas mixture.

To the student of colloid chemistry, considered from its simplest aspect—the physical and chemical activity of finely divided matter—smokes provide a comparatively simple system for investigation.

To obtain the data necessary for a quantitative study of the formation and behaviour of these gaseous disperse systems, it has been found necessary to develop a special experimental technique. This has been done with remarkable skill and ingenuity by the authors of the book under review.

The book opens with an introductory discussion of the nature and structure of smoke and an account of the earliest systematic attempts, made some fourteen years ago, to determine the mass concentration of smokes, the size of the particles and the number of particles per unit volume, and the way in which these characteristic quantities change with time. These early methods were subject to error, owing to the difficulty of illuminating sufficiently all the particles in the field of the ultramicroscope.

The improved methods that have been developed by the authors are described, and a full account is given of the ingenious method of H. L. Green, in which the ultramicroscopic visibility of the very fine particles is increased by condensing water vapour upon them, while the errors due to faulty observation are eliminated by actually photographing the particles within the field of view.

The authors show how the experimental methods can be applied to the systematic study of smoke coagulation, and a theory of coagulation, based upon that of Smoluchowsky for homogeneous sols, is developed and shown to be adequately justified by the experimental data.

The authors adopt two methods of smoke formation: In the first, they dilute and chill a small quantity of the hot vapour of a high boiling-point substance, such as stearic acid or resin, with a blast of cold air. In the second, they blow a gentle stream of air across an arc struck between poles of metals such as zinc, cadmium or magnesium. They point out that von Weimarn's theory cannot be applied satisfactorily to the study of smokes formed in this way since, during the formation of the smoke, the temperature is continually changing, and with it the degree of supersaturation. Possibly, however, the theory might be applied usefully to the study of smokes formed by chemical interaction between two gases such as ammonia and hydrogen chloride. Using such a method, the initial concentrations and the temperatures and pressures of the two gases could be varied widely, and the effect of other gases and vapours upon the nature of the particles formed could be investigated. By this means, possibly, the early stages of particle formation could be controlled more completely and the effect of individual factors observed more accurately. It would be interesting to know why the authors decided not to use this method of smoke formation.

One of the most interesting chapters in the book is that which deals with the growth and structure of smoke particles of different substances. Apparently, the ultimate form of a smoke particle, whether crystalline, spherical or chain-like, depends primarily upon the temperature at which the smoke is formed, the rate of crystallisation of the material and the way in which the primary particles are electrified.

A very full account is given of the technique employed for the determination of the weight concentration of the smoke, of the size and density of the individual particles and their size distribution in the smoke. The scattering of light by smokes and the curious phenomenon of photophoresis are well described. Other important chapters deal with the electrification of smoke particles and with the evaporation of small droplets. The book concludes with a stimulating and suggestive chapter, indicating some of the lines along which further research might profitably be carried out.

The authors have carried out a fine piece of pioneer investigation with conspicuous success. The book is valuable for the clear and full description which it contains of their experimental methods and of the way in which they can be applied to the study of the formation and the behaviour of smokes. The book can be recommended heartily to all who are interested in smokes, either from the purely physico-chemical standpoint or from the standpoint of the chemical engineer—that applied physical chemist—who so often is called upon to control smoke-producing reactions, to clarify turbid gases and vapours or to manufacture finely divided pigments and catalytic substances from gases. The book is written in a lucid and interesting manner; it is well illustrated, and can be thoroughly recommended as a stimulating introduction to a new and fascinating field of investigation.

W. E. Gibbs

Von Davy und Döbereiner bis Deacon. *By A. Mittasch and E. Theis. 23 × 16 cm; pp. 278. Berlin: Verlag Chemie, 1932. Price: 18.50 marks.* The potentialities in the applications of surface catalysis to industrial problems of the most varied character were probably first realised to the greatest extent in those varied German undertakings now represented by the I. G. It is a graceful appreciation of this fact that has prompted Dr. A. Mittasch (of the research laboratory at Oppau) and Dr. Theis to celebrate the close of the first fifty years of scientific attainments in this field by presenting us with this volume. The historical development of the subject during these early years is entwined around the names of a few distinguished men and these have been used to focus our attention both on the advances and on the difficulties contracting the pioneers.

During the last fifty years the number of papers which have appeared in the scientific press dealing with the subject of catalytic oxidation must run into the hundreds if not thousands. In all probability few, if any, of the writers of these papers have troubled to read, far less re-read, the work of Davy and Döbereiner and the subsequent work of Faraday and Schönbein. In the United States, Professor Bancroft has called attention again and again both to the importance of and interest to be found in such reading and our thanks are due to these authors in adopting this method of sketching the historical development of such an interesting subject.

Amongst other names included in the text are to be found those of Thénard, Berzelius, Liebig and Mitscherlich, whilst the early technical development of the subject is presented to us in the form of an account of the origins of the sulphuric acid contact process, and synthesis and oxidation of ammonia and the Deacon process.

The book is very readable, well printed and contains the portraits of sixteen distinguished men.

Eric K. Rideal

Lichtelektrische Zellen und ihre Anwendungen. *By H. Simon and R. Suhrmann. 22 × 15 cm: pp. viii + 373; Berlin: Julius Springer, 1932. Price 33 marks, bound 34.80 marks.* I am really the last person who ought to review this book, for I am part author of the only English (as distinct from American) book likely to come into competition with it. But I must do my best, and leave the authors of the book and the readers of this journal to complain to the Editor of my inevitable deficiencies.

The difficulty in writing a book on photoelectric cells is that the audience addressed is so indeterminate. It is almost impossible to cater in a single volume for the pure theorist, the manufacturer, the experimenter, the engineer, the picture-telegraphist and talking film expert—and lastly the omnivorous person prepared to read about anything that he thinks new. There are only two alternatives open. One is to cater for all readers; the other to cater definitely for a single class and to neglect steadfastly all the rest. This second alternative is not as easy as it sounds; for the spheres of interest of different classes overlap, and the author, having entered a sphere in the interest of one class, is apt to explore it too far in the interests of another. Certainly neither Zworykin and Wilson nor Campbell and Ritchie have wholly mastered the difficulty; perhaps that is why Drs. Simon and Suhrmann have preferred the first alternative.

For both their preface and their list of contents indicate that their aim is to be encyclopaedic. They take credit that they have dealt much more fully than our books with theory, with manufacture, and with apparatus auxiliary to photoelectric research, and yet they have not abandoned wholly any of the matters with which we dealt; their section-headings cover every subject suggested by their title. As an encyclopedia then I propose to judge the book.

The merits required of an encyclopedia are completeness and accuracy. Let us test it on this score. Here is a list of the more important matters omitted. In their theory there is no mention of quantum mechanics. In methods of manufacture there is no hint of how to prepare the type of cell that now forms 90% of the output of "alkali metal" cells, at least in America and England. In fact I am not sure that this cell is even mentioned (for it is not always clear what a "caesium" cell means), although its cathode, produced by heating oxidised Ag in Cs vapour, is much more sensitive to white light than any other. There is no account of the selenium "Sperrschicht" cell, although it seems likely to replace the cuprous oxide cell to which many pages are devoted. For the cathode of cells to measure "erythema radiation" there is no mention of Li or Ur, both of which are claimed to be vastly superior to Cd, which they recommend. Under sources of ultra-violet light they mention neither the continuous H_2 spectrum or that of bombarded Th. "295 Abbildungen in Text" (including one photograph of a stop-watch and two of monochromators) are poor consolation for these omissions.

Inaccuracy in major matters is more difficult to establish; for authors so eminent as these are not likely to make mere blunders in strictly scientific matters. But in many cases conciseness seems to me pushed to the point where it becomes very misleading. But it is sometimes said: Inaccurate in one thing, inaccurate in all; let us test a minor matter then. The footnotes of the book are full of the orthodox "references," tabulated in the name-index. I naturally turn to my own name. 6 entries here. Of these one confuses me with Campbell-Swinton, who is not tabulated; another refers to a diagram, due to Clayton Sharpe, and representing an arrangement against which I have always mildly protested. 33% errors at a random trial.

Truly and honestly I should like to find countervailing virtues on which I could descant. One undoubtedly there is. Being the latest book, it is more up-to-date than any other; it includes, for instance, something about the very important Sperrschicht cells, which the older books hardly mention. But there my list ends. Lucidity cannot be included, and many readers will feel diffident about critical judgment when they observe how much space is given to the authors' own work. However all this is doubtless due to my prejudice —and so I had better stop. Since I wrote this Hughes and Du Bridge's book has appeared!

Norman R. Campbell

Hydrogen Ions. *By F. T. S. Britton. 22 × 14 cms. Pp. xvi + 589. London: Chapman and Hall, 1932. Price: 52 shillings.* That a second edition of Dr. Britton's work on hydrogen ions should be called for in less than three years after the appearance of the original edition, is, in itself, evidence of the popularity and merit of the book. The book deals with acid and alkali titrations and p_H measurements by the potentiometric and indicator method. Full accounts are given of the theoretical and practical details of both methods. The importance of p_H measurements in many industries (leather manufacture, chrome and mineral tanning, vegetable tanning, sugar manufacture, pulp and paper manufacture, brewing, baking, water purification, and soil fertility) is described at great length. The new edition is some 74 pages larger than the original edition, which is mainly due to the inclusion of new chapters on (i) "Recent theories of electrolytic solutions. The influence of neutral salts," (ii) The precipitation of sulphides, (iii) The hydrogen ion concentration of eggs. The new thermionic value circuits of Stadie, Harrison and others for potentiometric titration are described in detail. These circuits overcome the uncertainties found in the original method of Goode. The Harrison system of value amplification by means of which the E.M.F. of high resistance glass electrodes can be measured with a galvanometer is also clearly described. The theories of Lewis, Debye, Hückel, Harned and others on ion activities and electrolytic solutions are summarised and discussed. The author has also added to the account of his own work on buffer mixtures, and also on the antimony, antimony oxide, tungsten and oxygen electrodes. An account is also given of the importance of hydrogen ion concentration in the precipitation of hydroxide and basic salts. Much of the work described here is due to the author and his collaborators; it is fundamental, interesting and of great practical importance. An important error has however crept in on p. 303, Table 83a. A list of solubility products of hydroxides calculated from the precipitation curves depicted on p. 301 is given. The method of calculation is quite inaccurate, but the rather amazing fact is that the calculated values of the solubility product are generally in fair agreement with the values recorded in the literature.

Apart from the blemish noted above the book is very good. It gives a really good account of the theory and technique of hydrogen ion determination. It is well-balanced and it is written in a pleasant and readable manner, it is well illustrated and indexed. It is a book which may be warmly recommended.

James F. Spencer

Experimental Cookery. *By Belle Lowe. 23 × 16 cm; pp. xi + 498. New York: John Wiley and Sons: London: Chapman and Hall, 1932. Price: $4.50.* A quotation of Ostwald's which Dr. Lowe has used in her introductory chapter concerning the relation of cookery to colloid chemistry is of such interest that I shall repeat it here. "Scientific study of the field still contents itself with chapters on analysis and the recognition of adulterants, but chapters dealing with the preparation of food are hardly started. Much as everyone would like to obtain better food for less money, study of such questions is regarded as menial and best left to the cook. A scientific study of the preparation of food is considered as only amusing even in scientific circles." These remarks were made in 1922.

The appearance of Dr. Lowe's book has supplied the *amused* scientist with information which is both obtained by and explained soundly on generally accepted colloidal principles. He may well stop being amused and devote himself to an interested study of the material she has presented. There are many of us who openly rejoice to have this material between two covers. No longer will certain classes need to grumble for an adequate text-book.

The arrangement of the book is logical and commendable; yet it is not necessary for the material to be used in just such a sequence. In the first chapter the author seeks to acquaint the student with the principles of colloidal chemistry which are of importance in the study of foods and food preparation. Unfortunately the majority of students in Home Economics have not had courses in even elementary Physical or Colloidal Chemistry; hence the tremendous importance of this first chapter. It is not a long chapter. After a general classification of substances based upon the degree of dispersion in solution, methods of lessening or increasing the degree of dispersion of substances in *food preparation* are discussed. Under the heading of Properties and Classes of Colloids based upon Physico-Chemical Relationships in Liquids, we find adequate discussion of reversible and irreversible colloids, colloid gels, swelling of gels, syneresis, coagulation of proteins, etc. In addition the chapter includes a discussion of boundary phenomena; fluidity, viscosity and plasticity of colloidal systems; energetics; and finally hydrogen ion concentration. It is an excellent summary—yet, as the author suggests, for the uninitiated student it would be a difficult chapter to digest. Either much lecture material must accompany its assimilation, or it should be, and probably better, utilized along with other chapters concerned with descriptive information regarding food and food manipulation. Otherwise such words as "cataphoresis" may be difficult, and the importance of adsorption may be underestimated. There are many apt examples selected for each of the subjects included.

Other chapters in the book have to do with sugar cookery, freezing and the freezing process, fruits and vegetables, jelly, gelatin, meat, emulsions, milk, egg cookery, wheat flour and bread, batters and doughs, and fats and oils. At the conclusion of each chapter there is an ample and well worked out group of pertinent experiments.

The preceding list of subjects covered in the various chapters indicates that the book is comprehensive. The chapter concerned with batters and doughs is of such excellence that it may be considered separately. Leavening agents are considered first, then the structure of batters and doughs. There follow specific remarks concerning the formation and structure of popovers, timbales and cover batters, cream puffs, griddle cakes, waffles, muffins, biscuits and cakes. The information is well arranged and extensive. The illustrations in this particular chapter consist of diagrammatic drawings, photographs and photomicrographs, each one carefully labelled and serving as evidence for some well-made point.

The photomicrographs moreover, showing the size and appearance of sugar crystals in fondants made by various methods, and standing over varying time intervals, as well as those concerned with emulsions made by varying the quantities of oil and vinegar are unusually helpful. Surely the microscope is one of the most useful instruments for such studies and the permanent records obtained easily via its camera attachments are becoming invaluable aids to the chemist.

Another tremendously desirable feature of the book is the accommodating list of references following each chapter—lists commodious, yet at the same time sufficiently abridged to form a most useful compendium.

It is perhaps unwise and unfair for me to select certain parts for a more detailed comment than the others. Such is not my intention. The book is the work of an expert—assisted by experts; and represents another combination of essential chemistry with facts. Such are welcome additions to our literature. *Irene H. Sanborn*

Solutions superficielles. *Fluides à deux dimensions, et Stratifications monomoléculaires. By André Marcelin. 24 × 16 cm; pp. 163. Paris: Les Presses Universitaires de France, 1931. Price: 80 francs.* M. Marcelin's volume is exactly described by its title and sub-title and represents a most valuable contribution to a subject which is, in many aspects, new and expanding, and which, moreover, has not been the subject of many monographs.

The author's development of the subject opens with a historical exposé, which, beginning with the fundamental observations of Miss Pockels, leads up to the developments made by Langmuir. He then proceeds to discuss the physical state of "solution superficielle," following this by a detailed and very useful account of the experimental methods employed. Space will hardly permit even of the mention of the titles of all the sixteen chapters of the book, but we may say that no point of outstanding interest is omitted, and that, among other matters, we find a full treatment of oleic acid and of the dimensions of its molecule, of pseudo-superficial solution, of applications of the Gibbs equation, of the effect of a surface film in lowering the Volta effect between an electrotype and a metal, and of black spots on films and of the thickness of *p*-toluidine crystals formed by solution or by sublimation.

M. Marcelin's clear and ordered account of the subject is very welcome and should find a place on the shelves of every physicist and chemist interested in the general properties of matter. *A. Ferguson*

2689

IRREVERSIBLE PROCESSES IN ELECTROLYTES. DIFFUSION, CONDUCTANCE, AND VISCOUS FLOW IN ARBITRARY MIXTURES OF STRONG ELECTROLYTES*

BY LARS ONSAGER AND RAYMOND M. FUOSS

1. Introduction

1.1. *Scope and Aims.*

In an electrolyte, the Coulomb forces between the ions will affect the thermodynamic and other physical properties of the system; these effects can be calculated, because the force law is known. The mathematical difficulties involved were first overcome by Debye and Hückel,[1] who derived limiting laws for the variation of molecular freezing-point depression, etc., and of molecular conductance with the concentration, c, all of the form

$$F(c) = F(0) - \alpha\sqrt{c} \qquad (1.1.1)$$

where $F(c)$ stands for any one of these properties, while $F(0)$ and α are constants. The term $-\alpha\sqrt{c}$ represents the influence of the ionic forces. It is characteristic of the theory that the factor α can be computed. For functions $F(c)$ describing irreversible processes, the value of α will in general depend on the (limiting) ionic mobilities; in addition, only the charges of ions and the ratios of their concentrations are involved, besides properties of the solvent (and universal constants).

The present work deals with conductance, diffusion and viscosity; explicit formulas of the type (1.1.1) are derived. Earlier computations, which were limited to electrolytes containing only two species of ions, will be extended to electrolytes of arbitrary composition, although the scope of the investigation is still limited by the condition that *the total concentration of ions must be low.* As a consequence of mathematical approximations, we shall obtain in the end asymptotic formulas of the type (1.1.1), while more exact computations, which we have not attempted on account of the mathematical complications involved, would, judging from tentative calculations, lead to expressions of the type

$$F(c) = F(0) + \alpha\sqrt{c} + \beta c \log c + \gamma c + \cdots \quad . \qquad (1.1.2)$$

The limiting $\sqrt{c}$ laws for the conductance and transference numbers of *simple electrolytes* (i.e. containing only two species of ions), have been computed by one of us in a previous treatise,[2] which amounted to a refinement of the original theory given by Debye and Hückel.[3]

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* Contribution from the Chemical Laboratory of Brown University.

[1] Debye and Hückel: I, Physik. Z., 24, 185 (1923); II, 24, 305 (1923).

[2] Onsager: I, Physik. Z., 27, 388 (1926); II, 28, 277 (1927).

[3] Debye and Hückel: II, loc. cit.

The only published computations for electrolytes of a more general composition have been given by Bennewitz, Wagner and Küchler,[1] who considered the case of a third ionic species present in very small quantity.

Within the limited scope outlined above, the modern electrostatic theory of electrolytes has performed remarkably well in accounting for a complex pattern of experimental data on the basis of a simple picture.[2] The present calculations extend the range of phenomena thus covered. The most interesting effect connected with electrolytic conduction in mixtures, as contrasted to simple electrolytes, was first observed experimentally by Bray and Hunt,[3] who measured the conductance of NaCl-HCl mixtures, and showed that the isoionic principle does not hold; that is, the conductances for a given total concentration of ions (and the same total "ionic strength") are not additive in this case. No corresponding effect is observed in the thermodynamic behavior of electrolytes, and curiously enough, the theory predicts for *simple binary electrolytes*, in accordance with an empirical rule due to Kohlrausch,[4] that the mobility of any ion at a given concentration is independent of its partner ion in the solution, e.g., Λ_{Cl} is the same in 0.01 *n.* HCl as in 0.01 *n.* KCl. In a HCl-KCl mixture, as we shall see in the following, the theory predicts that the fast H^+ ions will be slowed down more than usual, while the slow K^+ ions, "stealing their thunder" as the ions migrate past each other, will be accelerated in proportion, and the Cl^- ions will move with (practically) their usual velocity. The nature of the effect was recognized by Bennewitz, Wagner and Küchler;[5] it has been demonstrated experimentally by these authors and by Longsworth.[6] The present computations permit a quantitative comparison between theory and experiment. When due allowance is given for mathematical approximations, which become rather serious for, say, 0.1 *n.* concentration, the experimental verification may be called satisfactory.

The investigation of diffusion is possibly the most important part of the present contribution to the theory of electrolytes. Here the main effect of electrostatic forces between the ions is a thermodynamic one: The gradient of the thermodynamic potential, which represents the "driving force" upon the ions, is less than it would be in an ideal solution for the same concentration gradient.[7] However, we shall see that the velocity of diffusion for a given "driving force" may also be affected by the electrostatic (and hydrodynamic)

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[1] Bennewitz, Wagner and Küchler: Physik. Z., **30**, 623 (1929).

[2] In this discussion we shall concentrate on the problem in hand, and make no pretense of doing justice to mass-action effects, or in general to specific interaction of ions. The procedure for taking such effects into account is fairly obvious; the questions involved have been taken up by several authors and have, by and large, been given adequate consideration. See N. Bjerrum: Kgl. Danske Videnskab. Selskab. Math. fysis. Medd., VII, No. 9 (1926); Gronwall, LaMer and Sandved: Physik. Z., **29**, 358 (1928).

[3] Bray and Hunt: J. Am. Chem. Soc., **33**, 781 (1911).

[4] Kohlrausch and Holborn: "Leitvermögen der Elektrolyte"; MacInnes and Cowperthwaite: Trans. Faraday Soc., **23**, 400 (1927).

[5] Bennewitz, Wagner and Küchler: Loc. cit.

[6] Longsworth: J. Am. Chem. Soc., **52**, 1897 (1930).

[7] At higher concentrations, where short range repulsive forces become noticeable, an increase may result. For thermodynamic properties of concentrated electrolytes, see Harned: Trans. Faraday Soc., **23**, 462 (1927) and Hückel: Physik. Z., **26**, 93 (1925) (theory).

interaction of ions. Where more than two species of ions are present, the latter effects gain in importance (because the condition of zero electric current no longer forces all ions to move with the same velocity). Fundamentally, the problems of diffusion and conduction belong together; we thereby consider the most general migration of ions. From this point of view, the special case of pure conduction is not entitled to any preference. The general problem offers no additional obstacles to the theory; on the contrary, the essential characteristics of the problem are more readily recognized by avoiding an unnatural specialization.

The most general description of the laws of diffusion (and conduction) in a multi-component system will be formulated. The theory of electrolytes furnishes a good example in that all the terms in the phenomenological equations are important. We shall only be concerned with the formulation of the differential equations, which even for a simple electrolyte lead to a variable constant of diffusion, and make no attempt to integrate them for any practical case. For an actual test of the theory it would seem necessary to carry out experiments in which the difference between the concentrations of the interdiffusing solutions were relatively small, so as to measure the *differential* coefficient of diffusion, which is considered by the theory.

The differential equations for diffusion take the simplest form when expressed in terms of "driving forces," namely the gradients of thermodynamic potentials.[1] A system of linear equations

$$-J_i = \sum_{k=1}^{s} \Omega_{ik} \operatorname{grad} \mu_k, \quad (i = 1, 2, \ldots, s), \qquad (1.1.3)$$

relate the velocities $v_1, \ldots v_s$ (relative to the solvent) of the different ionic species to the gradients of the *total potentials*

$$\mu_i = \mu'_i + e_i\psi, \qquad (1.1.4)$$

where μ_i is the ordinary thermodynamic potential of Gibbs, ψ the electrostatic potential, and e_i is the charge per unit amount of a species of ions. As pointed out by Guggenheim and others,[2] only the sum (1.1.3) enters into thermodynamic relations, and into the laws of diffusion. The matrix Ω is symmetrical:

$$\Omega_{ik} = \Omega_{ki}. \qquad (1.1.5)$$

This symmetry relation, which is responsible for a well-known relation between transference number and electromotive force of a concentration-cell with transference,[3] is not a thermodynamic theorem,[4] but it can be derived

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[1] Cf. W. Nernst, who expressed the driving forces in terms of osmotic pressure, which is directly related to thermodynamic potentials. Nernst: Z. physik. Chem., 2, 613 (1888). The thermodynamic relations in question have been discussed by N. Bjerrum: Z. physik. Chem., 104, 406 (1923).

[2] Guggenheim: J. Phys. Chem., 33, 842 (1929); 34, 1540, 1758 (1930); J. Am. Chem. Soc., 52, 1315 (1930); P. B. Taylor: J. Phys. Chem., 31, 1478 (1927).

[3] H. v. Helmholtz: Wied. Ann., 3, 201 (1876); Wiss. Abh. 1, 840; MacInnes and Beattie: J. Am. Chem. Soc., 42, 1117 (1920).

[4] Cf. J. W. Gibbs: "Collected Works" I, 425 (1928); W. D. Bancroft: J. Phys. Chem., 7, 416 (1903).

from the very reasonable assumption that molecular dynamical systems, like those known to our macroscopic experience, possess symmetry in past and future.[1]

The following computations will be based on certain fairly general assumptions regarding the mechanism of resistance to migration of ions. The assumed mechanism is compatible with the principle of microscopic reversibility, and, as one should expect, the results conform to (1.1.5). An alternative form of (1.1.3), incorporating the symmetry relation (1.1.5), is obtained by the construction of a "dissipation-function."

The problem of viscosity has been included in this treatise mainly because it yields to the same mathematical methods as the conductance-diffusion problem; we thereby avoid a duplication of the calculations, which are to a great extent identical for both problems. The electrostatic contribution to the viscosity η of an electrolyte obeys the formula

$$\eta(c) - \eta(0) = \alpha\sqrt{c}, \qquad (1.1.6)$$

as has been shown by earlier calculations and experiments[2] by other authors for simple electrolytes. In extending the theory to cases where 3 or more species of ions are present, we find that no new spectacular effects are to be expected. In some respects, the present treatment of the viscosity problem brings simplification as compared to previous computations. In regard to the physical picture, we disagree with Falkenhagen[3] on one detail which, fortunately, does not affect the result for viscosity. He considers cases where the velocity gradients for the ions differ from the gradient for the solvent and, in our opinion, a material difference cannot occur. Falkenhagen arrived at his conclusion in searching for a mechanism of force transfer between ions and solvent. We have therefore investigated the mechanism of force transfer, an interesting problem in itself (although a barren one for experimenters), and we can show that there must indeed be a motion of ions relative to the solvent, but of another type than that suggested by Falkenhagen: The transfer of force that takes place in any given volume element, and consequently the local flow density of ions relative to the solvent, will be *proportional to the divergence of the velocity gradient.* In addition, there may be a transfer of force in the boundary layer; in the simplest case of a constant velocity gradient, the entire transfer of force takes place along the boundary.

1.2. *Present and Possible Future Advances in Mathematical Methods.*

In the present work, certain mathematical methods which are well known to other branches of theoretical physics will be applied for the first time to the theory of electrolytes. On this basis alone a brief survey of mathematical methods seems advisable and we have another, more important reason: while the scope of the present computations will be limited so as to obtain only the

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[1] Onsager: Phys. Rev., **37**, 405 (1931); **38**, 2265 (1931).

[2] Grinnell Jones and M. Dole: J. Am. Chem. Soc., **51**, 2950 (1929); Falkenhagen and Dole: Z. physik. Chem., **6**, 159 (1929); Physik. Z., **30**, 611 (1929); Falkenhagen: Physik. Z., **32**, 365, 745 (1931).

[3] Falkenhagen: Physik. Z., **32**, 365 (1931).

first ($\sqrt{c}$) term of the expansion (1.1.2) correct, we believe that a refinement of these calculations would be practicable, though laborious, and we have definite ideas about the procedure.

The computation consists of two parts: first (in section 2), the derivation of fundamental equations for the "ionic atmospheres," simplified by certain approximations, and, second (in sections 3 and 4), the specialization and the solution of the fundamental equations for the different cases to be considered, namely the problem of viscosity and that of conduction and diffusion.

The derivation of the fundamental equations will be complete in itself, and accessible to a reader familiar with the theory given by Debye and Hückel for the thermodynamic properties of electrolytes, which comprises the "statics" of the ionic atmosphere. We believe that a certain measure of simplification as compared to a previous treatise[1] will be welcome.

Full mathematical rigor is a distant ideal for the theory of electrolytes, but in our opinion, some advances towards this ultimate goal are possible.[2] It is already very difficult to justify rigorously inevitable approximations, and to establish an upper limit for the error thus introduced. The "static" theory of an electrolyte in thermodynamic equilibrium has been carried further,[3] but even there, the so-called "fluctuation-terms" in the differential equations are neglected,[4] and the effect of these terms is very difficult to estimate. Tentative calculations of our own tend to show that the "fluctuation-terms" are of minor importance, but it would be necessary to go more carefully into the question.

For the time being, it would be a great advance, in a certain sense a completion of the electrostatic theory (dealing only with Coulomb forces), if a method could be devised to compute the fields of the "ionic atmospheres" by a series of successive approximations, making it reasonably certain that the method would converge to the desired result, even though a mathematical proof of the convergence might be too much to ask.

In this sense, the original calculations of Debye and Hückel, and for the theory of irreversible processes those of the present work, may be considered as a first step in a series of approximations, which proceeds by developing the potential in the neighborhood of one particular ion, *or a pair, triple, etc. of ions*[5] in a power series of its charge (their charges). The distribution-functions can likewise be developed in power series. The two sets of functions are combined (in the "static" case) by the Boltzmann principle and the Poisson equations, and the terms in the power series can be calculated successively, whereby each

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[1] Onsager: Loc. cit.

[2] We are only concerned with the mathematical aspects of the derivation, and not as yet with the question of designing a physical picture that will account properly for all experimental results. Until we have a mathematically reliable theory, leading to definite conclusions on the basis of a reasonable picture, we do not know whether the experiments test the physical picture or merely our mathematical dexterity, or possibly a deceptive compensation of both.

[3] Gronwall, LaMer and Sandved: Physik. Z., 29, 358 (1928).

[4] R. H. Fowler: Trans. Faraday Soc., 23, 434 (1927); L. Onsager: II, loc. cit.

[5] By considering the neighborhoods of pairs, triples, etc. of ions, it is possible to *evaluate the fluctuation terms.*

new term may add corrections to the preceding. This method looks promising from the point of view of convergence, because the functions to be calculated, qua functions of the charges, are probably entire functions, whose series converge like e^x. It also seems probable that the method can be generalized to deal with irreversible processes, whereby the equation of continuity, which is the condition for a stationary state (in a statistical sense), replaces the Boltzmann principle. In applying this method of computation to electrical conduction, a complication arises because the external force on an ion is proportional to its charge. The complication is only apparent, and may be disposed of by replacing the electrostatic force temporarily by an arbitrary field of forces, which is not supposed to be a function of the charge, until the necessary approximations have been made. This procedure, which will be employed in the following, is necessary in order that the simplicity and the self-consistency of the principle of approximation become evident. As a further means of emphasizing the uniform character of the calculations, all approximations will be introduced before specialization to particular problems: viscosity and conduction + diffusion. In fact, a starting-point for calculating conductance in strong electric fields (Wien-effect), as given by Joos and Blumentritt,[1] may be found in our (2.5.7), which contains the approximations referred to, but which is not as yet specialized for weak fields. Likewise, the dispersion of conductance, as calculated by Falkenhagen, may be obtained from our calculations by retaining in the equation of continuity the left-hand member $\partial f/\partial t$ (instead of O), throughout the derivation.

In order to obtain a wieldy *solution* of the differential equations for the ionic atmospheres, we shall introduce matrix notation. Once this powerful mathematical tool is applied, we can deal with a system of linear differential equations as if it were one, and the intended generalization from an electrolyte containing only 2 species of ions to the case of s species becomes practically trivial. Moreover, this is the only way to obtain solutions that are formally compact, and even the methods for *a numerical computation* are most easily derived from the final results as they appear in matrix notation.

For a possible future refinement of the calculations along the lines indicated above, it will be necessary to know the solution of the equations that appear in the first approximation for the general case of s ions, because the principle of the method is to develop the potentials, etc. pertaining to each ionic species in power series of their charges, which implies variable charge and therefore variable species. (In order to accomplish anything with the fictitious ions involved in this method of computation, we must be able to deal with real ones.)

1.3. *Outline of the Physical Picture.*

As shown by Debye and Hückel, the effects of the Coulomb forces between the ions on the properties of electrolytes depend on the electric forces preventing a random arrangement of the ions in the solution. Instead, each positive

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[1] Joos and Blumentritt: Physik. Z., **28**, 836 (1927); Compare also Falkenhagen: Physik. Z., **32**, 353 (1931).

ion will surround itself with an "atmosphere" containing on the average more negative ions and less positive ions than the bulk of the solution, thus inducing a negative charge density in its neighborhood, while a negative ion will surround itself with a positively charged "atmosphere."

The total (mean) electric charge of an ionic atmosphere equals that of the central ion, with opposite sign, which suffices exactly to consume the force lines from the ion, so that its electric field beyond the bounds of the atmosphere is completely screened off.

The most important quantity characteristic of the ionic atmosphere is its mean radius, which can be calculated from the equilibrium between electric attraction and thermal agitation to be approximately $1/\kappa$ where

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{k=1}^{s} n_i e_i^2 . \qquad (1.3.1)$$

Here the electrolyte is supposed to contain ions of the species $1, \ldots, s$ with the charges $e_1, \ldots, e_s$ in the concentrations $n_1, \ldots, n_s$, while D denotes the dielectric constant, T the temperature, and k Boltzmann's constant, the gas constant per molecule. For the potential in the neighborhood of an ion of charge e_j Debye and Hückel have derived the formula

$$\psi_j = \frac{e_j}{D} \frac{e^{-\kappa r}}{r} \qquad (1.3.2)$$

which may be compared with $\psi = e/Dr$ for an isolated ion. According to (1.3.1), the inverse mean radius κ of the atmosphere is proportional to the square root of the concentration n, or exactly to

$$(\Sigma n_i z_i^2)^{1/2}$$

where $z_1, \ldots, z_s$ are the valences of the ions; hence the frequent occurrence of the power $n^{1/2}$, as in (1.1.1), in the theory of electrolytes. For instance, on the basis of (1.3.2), the potential at an ion due to its atmosphere will be

$$\psi_j = -\kappa e_j,$$

and this quantity determines the electrostatic contribution to the thermodynamic potential of an ion, which is

$$\Delta\mu_j = \frac{1}{D} \int_{\epsilon=0}^{\epsilon=e_j} \bar{\psi}(\epsilon)\, d\epsilon = -\frac{\kappa e_j^2}{2D} .$$

The numerical value of κ for a univalent binary electrolyte in water at 291° abs. amounts to

$$\kappa = 0.332 \times 10^8 \sqrt{c}$$

where c is the concentration in mols/liter. Thus for $c = 0.1$, $1/\kappa = 10^{-7}$ cm. and for $c = 1$, $1/\kappa = 3 \times 10^{-8}$ cm.

Two other quantities of the dimension length are of interest in the theory of electrolytes, namely the diameter a of an ion, for small univalent ions in water usually in the range

$$2 \times 10^{-8} < a < 4 \times 10^{-8} \text{ cm},$$

and the distance

$$d_0 = e^2/DkT, \tag{1.3.3}$$

at which two ions of charge e have the mutual potential energy kT. For univalent ions in water, approximately,

$$d_0 = 7 \times 10^{-8} \text{ cm}.$$

The approximations employed in the following computations, as well as (1.3.2), will be admissible[1] as long as the radius $1/\kappa$ of the ionic atmosphere is large compared to a and d_0; according to (1.1.1), this is indeed the case for sufficiently low concentrations. It is seen from the numerical data given above that for a univalent binary electrolyte in water, $1/\kappa = d_0$ for a molar concentration $c = 0.2$ and $1/\kappa = a$ for a concentration c near 1.0.

We shall discuss one more quantity of general interest pertaining to the ionic atmospheres, namely the *time of relaxation*. The importance of this quantity for irreversible processes in electrolytes has been emphasized already by Debye and Hückel. When the ions in the electrolyte migrate under the influence of an electric field (conduction) or a concentration gradient (diffusion), the symmetry of the ionic atmospheres will be disturbed in a manner that one may visualize by considering one ion under the influence of an external force: The ion will try to run away from its atmosphere, which becomes asymmetric with respect to the central ion.

A velocity gradient present in a moving electrolyte will cause a somewhat different type of disturbance: In laminar motion, spheres are deformed into ellipsoids, and the ionic atmospheres will assume a corresponding asymmetry.

Now the "normal" structure of an ionic atmosphere is an equilibrium between electric forces and thermal agitation of the molecules. These agencies are continually operating, and will tend to restore equilibrium after every disturbance.

The *time* τ that is necessary for this process of *relaxation* is given by the linear dimensions of the region in question, here $1/\kappa$, and the coefficient of diffusion, which equals kT/ρ where ρ is the frictional force on an ion moving with unit velocity.

On the basis of the general equation for diffusion

$$\frac{\partial c}{\partial t} = \frac{kT}{\rho}\frac{\partial^2 c}{\partial x^2}$$

the time of relaxation becomes

$$\tau = \frac{(1/\kappa)^2}{(kT/\rho)} = \frac{\rho}{\kappa^2 kT}. \tag{1.3.4}$$

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[1] Our description of the part of the ionic atmosphere that is inside d_0 (and a) will be inaccurate; but as long as $1/\kappa >> d_0$, the interior region ($r < d_0$) of the atmosphere is negligible compared to the rest. The approximations in question, which partly compensate each other, amount to neglecting higher terms in a power series expansion of $\exp(w/kT)$, where $w = e^2/Dr$ is the potential energy of a pair of ions, and in allowing impossible distances ($<a$) between ions.

except for a possible numerical factor of the order of magnitude unity. For the case of KCl in water at a temperature 291° abs. the above formula yields

$$t = \frac{0.55}{c} \times 10^{-10} \text{ sec.}$$

On account of this finite time of relaxation, a disturbance operating at a constant rate, such as migration of the ions, will maintain a constant deformation of the ionic atmosphere. On general principles, the resulting forces tend to oppose the causative disturbance; hence the Coulomb forces in the ionic atmospheres will yield contributions to the electrical resistance, the viscosity, etc., of the solution. The magnitude of such effects, and also of another effect, the "electrophoresis," which modifies the migration of the ions, will be discussed separately in dealing with the different phenomena. First, the fundamental equations for the process of relaxation will be derived.

2. Fundamental Equations for the Ionic Atmospheres

2.1. *The Distribution Functions.*

We are given a solution containing per cm³ $n_1, n_2, \ldots, n_s$ ions of species $1, 2, \ldots s$ with charges $e_1, e_2, \ldots, e_s$ e.s.u. per ion. Our problem is to find the limiting laws which describe an irreversible process such as electrolytic conductance, diffusion or viscous flow which may occur in the solution. The idea underlying the modern theory of electrolytes is that the presence of any particular ion at a given point in the solution will affect the chance of finding any other ion at a near-by point; in other words, the space distribution of ions cannot be entirely random as is presumably the case for an uncharged solute. We therefore shall need for our discussion a function which will give the chance of finding any two ions in two particular volume elements in the solution. This function may be specified by the following consideration.

Let two volume elements $dV_1 = dx_1\, dy_1\, dz_1$ and $dV_2 = dx_2\, dy_2\, dz_2$ in the solution be located by vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ drawn from an arbitrary origin. (See Fig. 1). The second is then located with respect to the first by means of the vector

$$\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1 = -\mathbf{r}_{12} \qquad (2.1.1)$$

(where the order of subscripts indicates the order of terms in the subtraction). For convenience in general discussions, we introduce for the components of $\mathbf{r}_1$ and $\mathbf{r}_2$ the notation

$$\begin{aligned} q_1^1 &= x_1, q_1^2 = y_1, q_1^3 = z_1 \\ q_2^1 &= x_2, q_2^2 = y_2, q_2^3 = z_2, \end{aligned} \qquad (2.1.2)$$

and shall mean by q_1^k (q_2^k) either x_1, y_1 or z_1 (x_2, y_2 or z_2) according to $k = 1, 2, 3$. Then

$$q^k = q_{21}^k = q_2^k - q_1^k = -q_{12}^k \qquad (2.1.3)$$

gives the coordinates of dV_2 with respect to an origin at dV_1. We shall also need temporarily a symbol to denote any one of the six coordinates $x_1, \ldots, z_2$; we shall use ξ_m for this purpose, where $m = 1, 2, \ldots,$ or 6.

We have postulated that the presence of an ion of a given species will affect the ionic concentrations in its vicinity; we indicate this explicitly by writing n_{ji} for the (time) average concentration of i-ions in the neighborhood of a j-ion. Now n_{ji} will in general depend on several variables, according to the situation to be investigated. (1) It will always depend on the distance r between the j-ion and the point where the concentration of i-ions is sought; (2) When forces act on the ions, a particular direction in space is specified, and n_{ji} will then depend on the direction of r; (3) Finally, if a variable velocity gradient is present in the liquid (viscosity), n_{ji} will depend on the location of the j-ion. Therefore

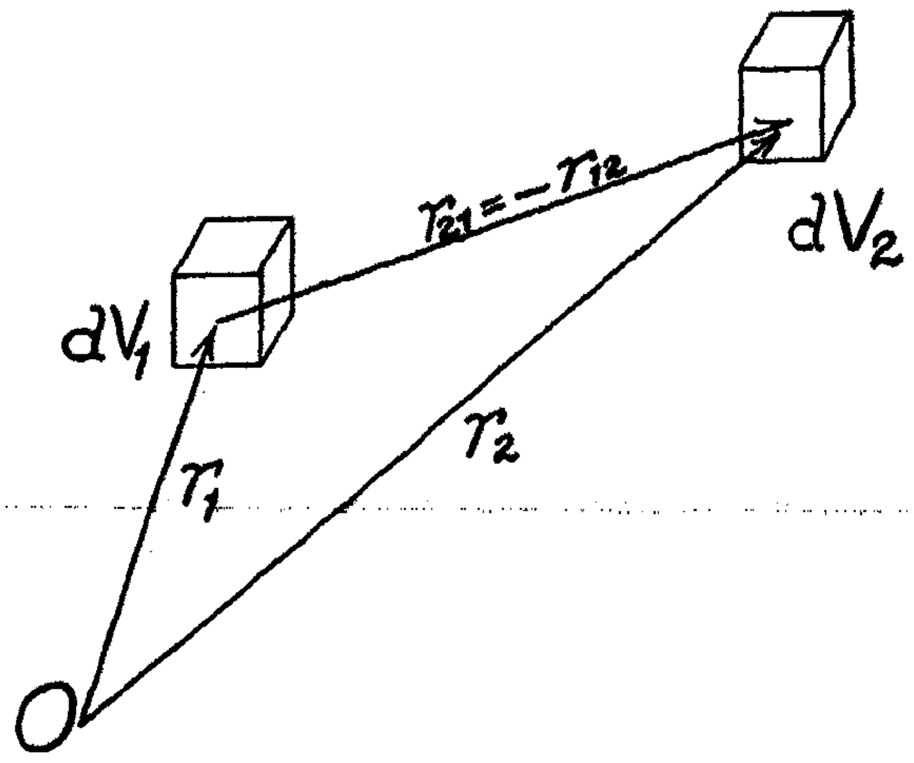

FIG. 1
Definition of Vectors

$$n_{ji} = n_{ji}\,(\mathbf{r}_1, \mathbf{r}_{21});$$

and likewise, (2.1.4)

$$n_{ij} = n_{ij}\,(\mathbf{r}_2, \mathbf{r}_{12})$$

gives the average concentration of j-ions at a distance $|\mathbf{r}_{12}|$ in the direction of $\mathbf{r}_{12}$ from an i-ion located by $\mathbf{r}_1$.

Now let us observe the pair of volume elements dV_1 and dV_2 ($\mathbf{r}_1$, $\mathbf{r}_2$ fixed temporarily) for a time t which is large compared to the time involved in the Brownian movement of the ions. We confine our attention to any two particular species of ions, say i and j. Our observations are made by means of three hypothetical clocks A, B, and C. Clock A starts each time a j-ion enters dV_1, and stops when the ion leaves so that the total time t_j recorded is the sum of the intervals out of the total observation time t during which a j-ion actually is in dV_1. Clock B starts when an i-ion enters dV_2 and stops when it leaves, and thus records the time t_i during which an i-ion actually is present in dV_2. Clock C starts when an i-ion enters dV_2 while a j-ion is in dV_1 or when a j-ion enters dV_1 while an i-ion is in dV_2 and stops when either ion leaves the corresponding volume element while the other ion remains in its element. Clock C thus records the time t_{ji} common to t_i and t_j, so that

t_{ji} is the total time out of t during which we simultaneously have a j-ion in dV_1 and an i-ion in dV_2. We then use the results of our experiment to compute the concentrations as time averages. We obtain

$$t_j/t = n_j dV_1,\ t_i/t = n_i dV_2;$$
$$t_{ji}/t_j = n_{ji} dV_2,\ t_{ji}/t_i = n_{ij} dV_1.$$

Eliminating t_j and t_i, we have

$$t_{ji}/t = n_j n_{ji} dV_1 dV_2 = n_i n_{ij} dV_2 dV_1. \qquad (2.1.5)$$

We may then use the relationship expressed in (2.1.5) to define our distribution functions, since they give the chance of finding simultaneously a j-ion in dV_1 and an i-ion in dV_2. Accordingly, we write

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_j n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_i n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}). \qquad (2.1.6)$$

We can now make more precise our picture of interionic action, supposing for a moment that a positive ion is fixed in dV_1. Then on the average, negative ions will enter dV_2 more frequently and therefore be present for a greater fraction of the total time, while positive ions will be scarce; this excess of negative ions persisting around the positive ion forms the so-called ionic atmosphere. In an undisturbed electrolyte, the atmosphere is obviously central-symmetric.

2.2. *The Equation of Continuity.*

We shall next investigate how f changes with time.[1] In order to consider this problem conveniently we plot in 6-dimensional space the coordinates $\xi_1, \ldots \xi_6$, so that specifying a point in 6-space specifies a pair of points in the solution, i.e., we can follow the behavior of dV_1 and dV_2 simultaneously by observing the volume element $d\xi_1 \ldots d\xi_6$. If we designate by $\mathbf{v}_{ji}$ the velocity of an i-ion in the vicinity of a j-ion, then

$$\mathbf{v}_{ji} = \mathbf{v}_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \qquad (2.2.1)$$

will in general depend on the location of both ions as well as on the location of the i-ion relative to the j-ion. Likewise,

$$\mathbf{v}_{ij} = \mathbf{v}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}).$$

The average components of velocity of a j-ion in dV_1 are $\dot{\xi}_1$, $\dot{\xi}_2$, $\dot{\xi}_3$ and of an i-ion in dV_2 $\dot{\xi}_4$, $\dot{\xi}_5$, $\dot{\xi}_6$ in 6-space. Now let us consider a 6-dimensional cube, whose center is at $\xi_1, \ldots, \xi_6$ and whose sides are of length $\Delta\xi_r$ ($r = 1, \ldots, 6$). Then if $\dot{\xi}_r$ is the *r-th* component of velocity at the center of the cube and $f_{ji}(= n_j n_{ji})$ is the concentration (in 6-space) at the same point, the flow of ions through a 5-dimensional face of the cube of area ΔS_r perpendicular to the ξ_r axis is

$$\left\{\dot{\xi}_r f_{ji} \pm \frac{\partial(\dot{\xi}_r f_{ji})}{\partial \xi_r} \quad \frac{\Delta\xi_r}{2}\right\} \Delta S_r,$$

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[1] The meaning of $\partial f/\partial t$ may seem obscure, since f is already defined as a time average. However, we may still ask for the "secular" change of this average in the course of a relatively long time. For the consideration of rapid changes (variation of conductance with frequency) the function f must be re-defined as an average over many similarly situated pairs of volume elements. Cf. Debye and Falkenhagen: Physik. Z., 29, 401 (1928).

so that the difference between influx and outflow for any pair of faces of the cube is $-\frac{\partial(\dot{\xi}_r f_{ji})}{\partial \xi_r}\Delta\xi_r \Delta S_r$ per unit time. Obviously $\Delta\xi_1 \ldots \Delta\xi_6 = \Delta\xi_r \Delta S_r$. Then the total contribution of all 6 pairs of faces gives the time change of concentration in the volume element

$$\frac{\partial f_{ji}}{\partial t}\Delta\xi_1 \ldots \Delta\xi_6 = -\sum_{r=1}^{6}\frac{\partial(\dot{\xi}_r f_{ji})}{\partial \xi_r}\Delta\xi_r \Delta S_r. \tag{2.2.2}$$

Dividing out the volume element, we have the equation of continuity, where the differentiation on the right gives a 6-dimensional divergence. But

$$\sum_r \frac{\partial}{\partial \xi_r} = \mathrm{div}_1 + \mathrm{div}_2,$$

where the subscripts 1 and 2 refer respectively to differentiation with respect to the components of $\mathbf{r}_1$ and $\mathbf{r}_2$. Since $f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})$ by (2.1.6), and $\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3$ $(\dot{\xi}_4, \dot{\xi}_5, \dot{\xi}_6)$ are the components of $\mathbf{v}_{ij}$ $(\mathbf{v}_{ji})$, (2.2.2) may be written

$$-\frac{\partial f_{ji}(\mathbf{r}_1, \mathbf{r}_{21})}{\partial t} = \mathrm{div}_1\,(f_{ij}\mathbf{v}_{ij}) + \mathrm{div}_2\,(f_{ji}\mathbf{v}_{ji}) = -\frac{\partial f_{ij}(\mathbf{r}_2, \mathbf{r}_{12})}{\partial t} \tag{2.2.3}$$

In any steady state, f is independent of time so that we obtain the stationary condition that

$$\mathrm{div}_1\,(f_{ij}\mathbf{v}_{ij}) + \mathrm{div}_2\,(f_{ji}\mathbf{v}_{ji}) = 0. \tag{2.2.4}$$

2.3. *The Equations of Motion.*

In our problems, three effects contribute to the motion of the ions: (1) forces on the ions, (2) thermal motion, (3) flow of the solution itself. If $\rho_i = 1/\omega_i$ is the friction coefficient of an ion of the *i-th* species, then a force $\mathbf{K}_i$ gives the ion a velocity $\mathbf{K}_i\omega_i$. We shall use the generalized equation[1] for Brownian movement to calculate the velocity due to thermal motion. The diffusion constant is assumed to be $kT\omega$ so that a concentration gradient will cause a current of strength $-kT\omega$ grad f. Then the average diffusion velocity is $-kT\omega$ grad ln f. If the bulk velocity of the solution at the point located by $\mathbf{r}_2$ is[2] $\mathbf{V}(\mathbf{r}_2)$, then

$$\mathbf{v}_{ji} = \mathbf{V}(\mathbf{r}_2) + \omega_i(\mathbf{K}_{ji} - kT\,\mathrm{grad}_2 \ln f_{ji})$$

gives the total velocity $\mathbf{v}_{ji}$ which appears in (2.2.4). We have written $\mathbf{K}_{ji}$ for the (mean) force which acts on an *i*-ion in the vicinity of a *j*-ion.

The equation of continuity specialized for a steady state now takes the form

$$\begin{aligned}&\mathrm{div}_1\,\{f_{ij}\mathbf{V}(\mathbf{r}_1) + \omega_j(f_{ij}\mathbf{K}_{ij} - kT\,\mathrm{grad}_1 f_{ij})\} + \\ &\mathrm{div}_2\,\{f_{ji}\mathbf{V}(\mathbf{r}_2) + \omega_i(f_{ji}\mathbf{K}_{ji} - kT\,\mathrm{grad}_2 f_{ji})\} = 0,\end{aligned} \tag{2.3.1}$$

where

$$\begin{aligned}f_{ji} &= f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), & f_{ij} &= f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) \\ \mathbf{K}_{ji} &= \mathbf{K}_{ji}(\mathbf{r}_1, \mathbf{r}_{21}), & \mathbf{K}_{ij} &= \mathbf{K}_{ij}(\mathbf{r}_2, \mathbf{r}_{12}).\end{aligned}$$

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[1] Debye and Hückel: II, loc. cit.

[2] We here neglect the hydrodynamic motion of the fluid at dV_2 caused by the presence of a moving *j*-ion at dV_1. This approximation amounts to dropping terms of the order $c \log c$ in the final results.

2.4. *The Results of Debye and Hückel for an Undisturbed Electrolyte.*

For the case of an electrolyte at rest under the action of no external forces, the ionic atmospheres are spherically symmetric with respect to the central ion, and the functions introduced above become pure functions of the distance $r = |\mathbf{r}_{21}| = |\mathbf{r}_{12}|$. We therefore write

$$f^\circ_{ji}(r) = n_j n^\circ_{ji}(r) = n_i n^\circ_{ij}(r) = f^\circ_{ij}(r) \qquad (2.4.1)$$

to indicate this situation.

An ion of charge e_j in a liquid of dielectric constant D produces a field derivable from the potential

$$e_j/Dr.$$

In an electrolytic solution, the fields due to the various ions superpose and any particular ion will be screened by the ions in its atmosphere. We designate by $\psi_j(\mathbf{r}_1, \mathbf{r}_{21})$ the potential due to an ion and its atmosphere in the general case and by $\psi^\circ_j(r)$ the same for the undisturbed case. The potentials are connected with the charge density

$$\sum_i n_{ji} e_i$$

by the Poisson equations

$$\Delta\psi_j = -\frac{4\pi}{D}\sum_i n_{ji} e_i \qquad (2.4.2)$$

$$\Delta\psi^\circ_j = -\frac{4\pi}{D}\sum_i n^\circ_{ji} e_i. \qquad (2.4.3)$$

If we assume that the concentration n°_{ji} of i-ions near a j-ion is determined from the energy[1] E_{ji} of an i-ion in the vicinity of a j-ion by the Maxwell-Boltzmann distribution, we have

$$n^\circ_{ji} = n_i \exp(-E_{ji}/kT). \qquad (2.4.4)$$

For this equilibrium, the average velocities must vanish, so that

$$\mathbf{K}_{ji} = \mathbf{K}_{ij} = kT \operatorname{grad} \ln f^\circ_{ji}. \qquad (2.4.5)$$

From (2.4.4), we find

$$kT \operatorname{grad} \ln f^\circ_{ji} = -\operatorname{grad} E_{ji} = -\operatorname{grad} E_{ij}. \qquad (2.4.6)$$

So far, no approximation has entered. If now we assume *linear* superposition of the potentials and consequently of the charge densities induced by two ions near one another (superposition of the atmospheres), we assume that $E_{ji} = e_i\psi^\circ_j$ and $E_{ij} = e_j\psi^\circ_i$. In other words, the average force acting on one ion is given by the potential of the atmosphere of the other. Then from (2.4.6), we see that our assumption leads to the result that

$$e_i\psi^\circ_j = e_j\psi^\circ_i$$

---

[1] E_{ji} is most simply defined by $\mathbf{K}_{ji} = -\operatorname{grad} E_{ji}$ to be the potential of the force $\mathbf{K}_{ji}$; according to (2.4.5), this force has indeed a potential. It is also possible to define E_{ji} as the net work of discharging an i-ion far away from the *particular* j-ion under consideration, moving it (without work) into the atmosphere of that j-ion, and recharging the i-ion at the distance r.

which means that the potential around an ion must be *proportional* to its charge;

thus
$$\psi^\circ_j = e_jF(r)$$

where $F(r)$ is independent of e_j. On the other hand, if we substitute $E_{ji} = e_i\psi^\circ_j$ into (2.4.4) and the latter into (2.4.3), we find

$$\Delta\psi^\circ_j = -\frac{4\pi}{D}\sum_i e_in_i \exp\left(-e_i\psi^\circ_j/kT\right)$$

but here, by hypothesis, the left member is linear in e_j while the right member evidently is not; hence our assumption has led to a contradiction. However, for small values of $e_i\psi^\circ_j$ we have

$$\exp\left(-e_i\psi^\circ_j/kT\right) \approx 1 - e_i\psi^\circ_j/kT \tag{2.4.7}$$

approximately, and if we allow this approximation, we obtain the linear equation

$$\Delta\psi^\circ_j = \kappa^2\psi^\circ_j \tag{2.4.8}$$

where
$$\kappa^2 = \frac{4\pi}{DkT}\sum_{i=1}^{s} n_ie_i^2. \tag{2.4.9}$$

The error which arises from terminating the power series for the exponential is small at great distances from the (j) ion, since ψ°_j is small. In the immediate vicinity of the central ion, namely for

$$r \leqslant d_0 = e_je_i/DkT$$

(cf. 1.3.3), the approximation is poor. However, for *low concentrations*, the radius $1/\kappa$ of the ionic atmosphere, which, according to (2.4.9), varies as $c^{1/2}$, becomes large and for $1/\kappa >> d_0$ the inaccurate description of the innermost region will cause a negligible error in our final results. Integration of (2.4.8) yields, considering the boundary conditions,

$$\psi^\circ_j = \frac{e_j}{D}\frac{e^{-\kappa r}}{r}. \tag{2.4.10}$$

This procedure was developed by Debye and Hückel. With the above approximation (2.4.7), the distribution function becomes

$$\begin{aligned} f^\circ_{ji} &= n_jn^\circ_{ji} = n_jn_i(1 - e_i\psi^\circ_j/kT) = \\ &= n_jn_i\left(1 - \frac{d_0e^{-\kappa r}}{r}\right) = n_jn_i\left(1 - \frac{e_je_i}{DkT}\frac{e^{-\kappa r}}{r}\right). \end{aligned} \tag{2.4.11}$$

2.5. *Perturbation of the Ionic Atmospheres.*

If a force acts on the ions in the solution under investigation, then there exists a preferred direction, and both distribution functions and potentials become asymmetric. We shall assume that the applied forces are small, so that we may consider the various functions to be changed by a small perturbation factor from their values in the undisturbed electrolyte. Accordingly, we set

$$\psi_j = \psi'_j\,(\mathbf{r}_1, \mathbf{r}_{21}) + \psi^\circ_j\,(r) \qquad (2.5.1)$$

$$f_{ji} = f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) + f^\circ_{ji}(r). \qquad (2.5.2)$$

For small forces, the (primed) perturbation terms will be proportional to the force. The asymmetric addition to the potential is connected with f'_{ji} by the Poisson equation:

$$\Delta\psi'_j = -\frac{4\pi}{D}\sum_i \frac{f'_{ji}e_i}{n_j} \qquad (2.5.3)$$

The perturbing force sets up an irreversible process in the solution, and the distribution naturally is no longer given by the Boltzmann equation. Hence the general condition (2.2.4) must apply, since $\mathbf{v}_{ji}$ no longer averages to zero. In accordance with the approximation principle of §2.4, we shall assume that the asymmetric addition to the field of a given ion is *proportional to the charge* of the ion, and that we may compute the field due to two ions by linear superposition of the separate fields. For the total force $\mathbf{K}_{ji}$ acting on an *i*-ion in the vicinity of a *j*-ion, we then have

$$\mathbf{K}_{ji} = \mathbf{k}_i - e_i\,\mathrm{grad}_2\,\psi_i\,(0) - e_i\,\mathrm{grad}_2\,\psi_j\,(\mathbf{r}_1, \mathbf{r}_{21}), \qquad (2.5.4)$$

where $\mathbf{k}_i$ is the applied external force, $-e_i\,\mathrm{grad}_2\,\psi_i(0)$ is the force due to the ion's own atmosphere and $-e_i\,\mathrm{grad}_2\,\psi_j$ is the force due to the *j*-ion and the latter's atmosphere. If we substitute (2.5.4) in (2.3.1), we obtain for the first term

$$\begin{aligned}\mathrm{div}_2\,(f_{ji}\mathbf{v}_{ji}) = \mathrm{div}_2(f_{ji}\mathbf{V}(\mathbf{r}_2) + \omega_i\big(f_{ji}\mathbf{k}_i - e_if_{ji}\,\mathrm{grad}_2\psi_i(0)\\ -e_if_{ji}\,\mathrm{grad}_2\,\psi_j(\mathbf{r}_1, \mathbf{r}_{21}) - kT\,\mathrm{grad}_2\,f_{ji}\big)\big). \qquad (2.5.5)\end{aligned}$$

In order to expand this, we note that $\mathbf{V}(\mathbf{r}_2)$ and $\mathbf{k}_i$ are divergence-free, and make the following simplifications. We neglect the term $\mathrm{grad}_2\psi_i(0)$ since (cf. 2.4.10) it is of the order e_i^2 while the other terms are of the order e_i. We replace f_{ji} in the $\mathrm{grad}_2\,\psi_j$ term by n_jn_i since $f_{ji} - n_jn_i \sim e_i$ and the term already has a coefficient e_i.
We thus obtain

$$\begin{aligned}\mathrm{div}_2\,(f_{ji}\mathbf{v}_{ji}) = \big(\mathbf{V}(\mathbf{r}_2), \mathrm{grad}_2\,f_{ji}\big) + \omega_i\big(\mathbf{k}_i, \mathrm{grad}_2\,f_{ji}\big).\\ -e_i\omega_in_in_j\Delta_2\psi_j - \omega_ikT\Delta_2\,f_{ji} \qquad (2.5.6)\end{aligned}$$

We now substitute (2.5.1) and (2.5.2) and note that for $\mathbf{k}_i = 0$, $\mathbf{v}_{ji} = 0$; hence the terms in f° and ψ° must cancel one another except in the two scalar product terms which vanish by hypothesis. We approximate f in these terms by f°. We thus obtain the equation of continuity (2.2.3) specialized to suit our particular problems in the form

$$\begin{aligned}&(\mathbf{V}(\mathbf{r}_2), \mathrm{grad}_2\,f^\circ_{ji}) + (\mathbf{V}(\mathbf{r}_1), \mathrm{grad}_1\,f^\circ_{ij}) +\\ &\quad\omega_i(\mathbf{k}_i, \mathrm{grad}_2\,f^\circ_{ji}) + \omega_j(\mathbf{k}_j, \mathrm{grad}_1\,f^\circ_{ij}) - e_i\omega_in_in_j\Delta_2\psi'_j\\ &\qquad -e_j\omega_jn_in_j\Delta_1\psi'_i - \omega_ikT\,\Delta_2f'_{ji} - \omega_jkT\,\Delta_1\,f'_{ij} = 0. \qquad (2.5.7)\end{aligned}$$

The first four terms of this equation contain the perturbing factors $\mathbf{V}$ and $\mathbf{k}$; the last four represent the asymmetric contributions to potential and distribution thereby produced. This gives us a system of s^2 differential equations connecting the s^2 distribution functions f'_{ji} with the s potentials ψ_j and the known function $f^\circ(r)$. Our general procedure in subsequent derivations will be to specialize (2.5.7) to a particular problem, eliminate the f'_{ji}'s by means of the Poisson equation (2.5.3) and solve the resulting system of differential equations for the s potentials ψ'_j.

3. Viscosity

3.1. *Description of Problem and Method.*

In this section, we shall consider a solution containing s species of ions and shall derive a relation giving the viscosity in terms of the various concentrations.

In order to define clearly the physical conditions of the problem, we shall review briefly the theory of motion in a viscous fluid, bearing in mind the fact that the fluid in question is an electrolytic solution, and shall first show qualitatively how the electrostatic forces between the ions will add to the forces transferred in such motion and estimate their order of magnitude. We picture the solution (see Fig. 2) confined between two parallel plates, h centimeters apart, of which the lower is fixed and the upper moves with constant velocity v' in the x direction, and shall assume for the moment a constant velocity gradient

$$\frac{\partial v_x}{\partial y} = \frac{v'}{h}$$

in the y direction, so that the velocity at the level y will be

$$v_x = (v'/h)y;\ v_y = 0,\ v_z = 0.$$

Recalling the definition of coefficient of viscosity η as the stress transferred per unit velocity gradient, a stress equal to

$$S_{xy} = \eta \frac{\partial v_x}{\partial y}$$

per unit area will be transferred from each layer of liquid to the layer beneath it. In the case of an electrolyte, we shall show that a part of this stress is due to electrostatic forces between the ions. In an undisturbed electrolyte, an ion of charge $+e$ will be surrounded by an atmosphere of total charge $-e$, situated at an average distance $(1/\kappa)$ in which the average distribution is spherically symmetrical since the ions have no preferred orientation. A velocity gradient in the liquid will deform a sphere into an ellipsoid, and the ionic atmospheres will be deformed accordingly. The electrostatic forces and the thermal motion, whose equilibrium determine the structure of the ionic atmospheres, will tend to restore the original structure, but this process of relaxation will not be instantaneous. If the relative rate of deformation is

$$\frac{\partial v_x}{\partial y}$$

and the time of relaxation is τ, a stationary deformation $\tau \frac{\partial v_x}{\partial y}$ will persist. In (1.3.4), it was shown that $\tau = \rho/(\kappa^2 kT)$. The deformation of the ionic atmosphere will then be of the order

$$\frac{\rho}{\kappa^2 kT}\,\frac{\partial v_x}{\partial y}. \tag{3.1.1}$$

Two ions of charge e, situated at a distance $(1/\kappa)$ exert a Coulomb force on each other equal to $e^2\kappa^2/D$ where D is the dielectric constant, so that the total transport of force (stress) between an ion and its atmosphere without regard to direction is $(1/\kappa)\,.\,(e^2\kappa^2/D) = e^2\kappa/D$.

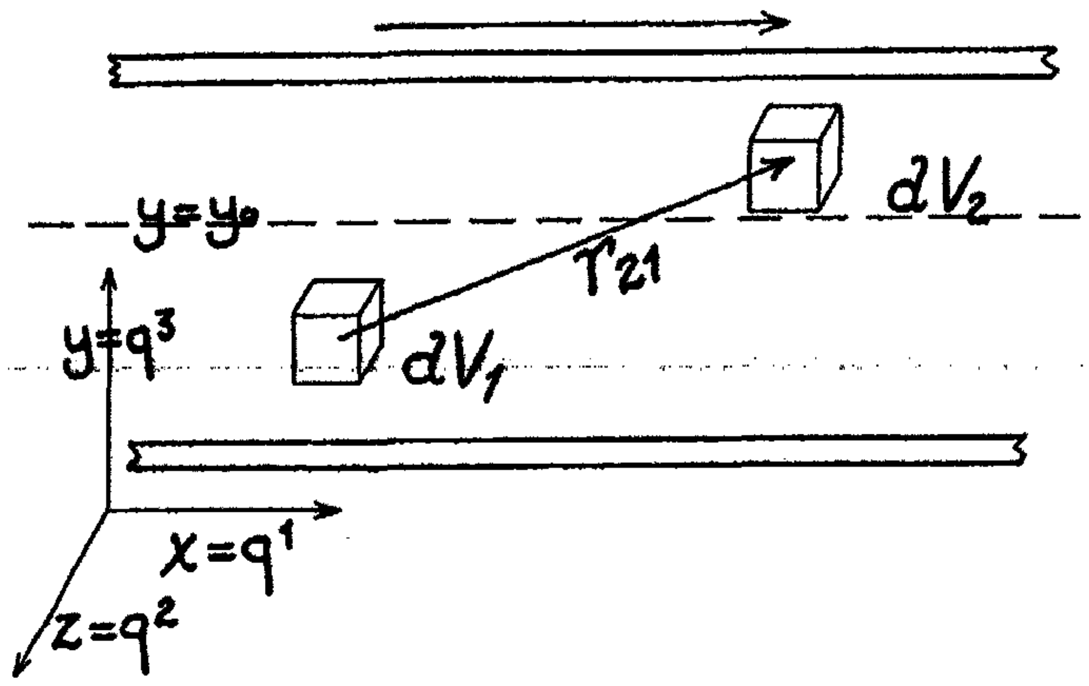

FIG. 2
Sketch for Viscosity Calculation

As long as the spherical symmetry of the ionic atmosphere is not disturbed, the stresses in different directions will compensate each other. A velocity gradient in the solution will cause a deformation of the order (3.1.1) as shown above, and we may expect that the resultant directed fraction of the total stress will be of the same order of magnitude. On this basis, the stress transferred between one ion and its atmosphere should be of the order

$$\frac{e^2\kappa}{D}\,\frac{\rho}{\kappa^2 kT}\,\frac{\partial v_x}{\partial y} = \frac{e^2\rho}{\kappa DkT}\,\frac{\partial v_x}{\partial y}$$

and that transferred by the interaction of $2n$ ions and their atmospheres of the order

$$\frac{ne^2\rho}{\kappa DkT}\,\frac{\partial v_x}{\partial y}$$

or, substituting (2.4.9) for κ^2 and allowing a numerical factor 8π,

$$S^*_{yx} \approx \kappa\rho\,\frac{\partial v_x}{\partial y}. \tag{3.1.2}$$

This result is expected to be correct except for a proportionality factor which must be evaluated by considering the exact type of deformation of the ionic atmospheres. Indeed, our final calculations yield for the case of s species of ions, where $\omega_1 = \omega_2 = \ldots = \omega_s = \omega = 1/\rho$, the stress

$$S^*_{xy} = \frac{1}{480\pi}\,\rho\kappa\,\frac{\partial v_x}{\partial y}. \tag{3.1.3}$$

This stress will be added to the stress transferred by friction between the solvent molecules, namely

$$S^0_{xy} = \eta_0\,\frac{\partial v_x}{\partial y}.$$

Consequently, the electrostatic forces cause an addition

$$\eta^* = \frac{1}{480\pi}\,\kappa\rho$$

to the viscosity η_0 of the pure solvent. The result of the above consideration is identical with that obtained by Falkenhagen.[1] The essential feature in (3.1.3) is the factor κ; on account of this factor the electrostatic contribution to viscosity varies as the square root of the concentration of ions. For example, for KCl at 25°C. in water,

$$\eta^* = 44.7 \times 10^{-6}\sqrt{c} = 5.0 \times 10^{-3}\eta_0\sqrt{c}.$$

For 0.1 n KCl, the electrostatic increase of viscosity amounts to 0.14% of η_0.

The electrostatic forces between ions will be transferred to the solvent by friction, whereby there must be a relative motion between ions and solvent. This relative motion may take place (in part) in the interior of the solution; however, as we shall show immediately, in certain cases, a relative motion of ions and solvent will take place only along the boundary, namely when the velocity gradient is constant throughout the interior.

If we now consider the general motion in a liquid where the velocity $\mathbf{v}$ at a point located by the vector $\mathbf{r}$ has components v_x, v_y, v_z, the y component of stress per unit area across a plane perpendicular to the x direction is

$$S_{xy} = \eta\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) = S_{yx}. \tag{3.1.4}$$

For a solution of electrolytes, two factors will contribute to the force transfer: first, the friction of solvent on solvent, and second, the interaction of the electrostatic forces between the ions. It is the latter which we wish to investigate. The equations of motion of an incompressible fluid are

$$\eta\Delta\mathbf{v} = \operatorname{grad} p - \mathbf{F} \tag{3.1.5a}$$

$$\operatorname{div}\mathbf{v} = 0, \tag{3.1.5b}$$

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[1] Falkenhagen: Loc. cit.

where p is the pressure and **F** the force per unit volume. If S°_{mn} is the general element of the stress matrix for motion in the pure solvent, then

$$S_{mn} - S^\circ_{mn} = S^*_{mn}$$

represents the average superposed stress due to ionic forces, and correspondingly

$$\eta - \eta^\circ = \eta^* \tag{3.1.6}$$

gives the increase in viscosity of the solution over that of the solvent. On introducing this into the equation of motion, there results

$$\eta^\circ \Delta \mathbf{v} = \operatorname{grad} p - (\mathbf{F} + \eta^* \Delta \mathbf{v}),$$

so that the effect of interionic forces may be interpreted as an addition to the volume force. Furthermore it is evident that wherever $\Delta \mathbf{v}$ vanishes in an interior region of the liquid, no force will be transferred from the ions to the solvent in that region. In the case of a constant velocity gradient, as in our example above, $\Delta \mathbf{v} = 0$ everywhere in the liquid. Still, the forces acting on the plates A and B (per unit area) equal $(\pm)\eta\ \partial v_x/\partial y$ and not $\eta^\circ \partial v_x/\partial y$. The difference $\eta^*\ \partial v_x/\partial y$ can be accounted for if we assume that the ions move relatively to the solvent along the boundaries (up to distances $1/\kappa$) and nowhere else, with a velocity that is sufficient to produce the required frictional force.

The flow of ions along a boundary is not easily calculated by direct methods although our consideration above shows that such an effect must be present. However, we shall calculate directly the relative motion of ions and solvent in the interior of the solution, that is, when $\Delta \mathbf{v} \neq 0$, and we shall show that the forces derivable from the potentials of the asymmetric "odd"[1] ionic fields agree with the term $\eta^* \Delta \mathbf{v}$ calculated from the stress S^*_{mn}. The contribution S^*_{mn} to the stress due to the presence of ions will be computed by the following method: By means of the Poisson equation (2.5.3) and the equation of continuity (2.5.7), we shall derive a system of differential equations which determine the potentials of the ionic fields, and give their solution for the general case of a mixture of s species of ions. Then S^*_{mn} will be computed as the average sum of the corresponding components of the electrical forces between all pairs of ions present, which will require the distribution function $f_{ji}(\mathbf{r}_{21}) = f_{ij}(\mathbf{r}_{12})$, giving the average concentration of i-ions in the vicinity of a j-ion and vice versa. By means of the Poisson equation, however, $f_{ji}(\mathbf{r}_{21})$ may be replaced by the potentials which have been obtained by solving the differential equations, and we shall have in explicit form the result desired.

3.2. *Evaluation of Velocity Terms in the Equation of Continuity.*

In accordance with the considerations of the previous paragraph regarding the nature of the velocity field, we shall expand the velocity as a Taylor series in the coordinates and neglect terms of higher order than the second, so

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[1] In the case of a constant velocity gradient, the potential in the ionic atmosphere is an *even* function of the distance in the sense that $\psi(x,y,z) = \psi(-x,-y,-z)$. A variable gradient will cause "odd" contributions to the field of the atmosphere.

that the velocity gradient will, to this approximation, be a linear function of the variables $q^1 = x, q^2 = y, q^3 = z$. We then have for the general component of the velocity at a point located by the vector $\mathbf{r}$

$$v^l(\mathbf{r}) = v^l(0) + \sum_{\lambda=1}^{3} q^\lambda \left(\frac{\partial v^l}{\partial q^\lambda}\right)_{r=0} + \tfrac{1}{2}\sum_{\lambda=1}^{3}\sum_{\mu=1}^{3} q^\lambda q^\mu \left(\frac{\partial^2 v^l}{\partial q^\lambda\, \partial q^\mu}\right)_{r=0}.$$

For convenience, we shall use the convention that Greek indices always imply summation, and introduce the following abbreviations:

$$a^l_m = \left(\frac{\partial v^l}{\partial q^m}\right)_{r=0}$$

$$b^l_{mn} = \left(\frac{\partial^2 v^l}{\partial q^m\, \partial q^n}\right)_{r=0} = b^l_{nm},$$

so that our expansion may be written compactly as

$$v^l(\mathbf{r}) = v^l(0) + a^l_\lambda\, q^\lambda + \tfrac{1}{2}\, b^l_{\mu\nu}\, q^\mu q^\nu. \tag{3.2.1}$$

For dealing with the motion in an ionic atmosphere, we shall find it convenient to shift the origin to a point $\mathbf{r}_1$, (specifying the position of the central ion). The velocity at another point $\mathbf{r}_2$ (where another ion might be found) will be

$$v^l(\mathbf{r}_2) = v^l(\mathbf{r}_1) + q^\lambda{}_{21} c^l_\lambda(\mathbf{r}_1) + \tfrac{1}{2}\, q^\mu{}_{21} q^\nu{}_{21} b^l{}_{\mu\nu}, \tag{3.2.2}$$

where $q^1{}_{21} = x_2 - x_1$, etc.
We identify the $c^l{}_m$'s by substitution of (3.2.1) for $v^l(\mathbf{r}_2)$ and $v^l(\mathbf{r}_1)$ into (3.2.2) and comparison of coefficients to be

$$c^l{}_m(\mathbf{r}_1) = a^l{}_m + b^l{}_{m\sigma} q^\sigma{}_1. \tag{3.2.2b}$$

The coefficients have the following properties by their definition:

$$a^\mu{}_\nu = a^\nu{}_\mu,\ c^\mu{}_\nu = c^\nu{}_\mu, \tag{3.2.3}$$

and the requirement that the solution be incompressible (3.1.5b)

$$0 = \operatorname{div} \mathbf{v} = a^\mu{}_\mu + \tfrac{1}{2}\, b^\mu{}_{\mu\nu}\, q^\nu + \tfrac{1}{2}\, b^\mu{}_{\nu\mu}\, q^\mu = c^\mu{}_\mu$$

gives the additional properties that

$$a^\mu{}_\mu = 0;\ b^\mu{}_{\mu\nu} = b^\mu{}_{\nu\mu} = 0;\ c^\mu{}_\mu = 0. \tag{3.2.4}$$

The velocity terms in the equation of continuity may now be evaluated. Since by definition (2.1.6) $f^\circ{}_{ji}(r) = f^\circ{}_{ij}(r)$ and $q_{21} = q_2 - q_1$, we have

$$\operatorname{grad}^l{}_2\, f^\circ{}_{ji}(r) = \left(\frac{\partial}{\partial q^l{}_2} f^\circ{}_{ji}(r)\right)_{r_1=\text{const}} = \frac{\partial}{\partial q^l{}_{21}} f^\circ{}_{ji}(r) \equiv D_l f^\circ{}_{ji}(r)$$

$$\operatorname{grad}^l{}_1\, f^\circ{}_{ij}(r) = \left(\frac{\partial}{\partial q^l{}_1} f^\circ{}_{ij}(r)\right)_{r_2=\text{const}} = -\left(\frac{\partial}{\partial q^l{}_{21}} f^\circ{}_{ij}(r)\right) \equiv -D_l f^\circ{}_{ij}(r)$$

Substitution of these and (3.2.2) in the velocity terms gives

$$\begin{aligned}((\mathbf{V}(\mathbf{r}_2), \operatorname{grad}_2 f^\circ{}_{ji}(r)) + (\mathbf{V}(\mathbf{r}_1), \operatorname{grad}_1 f^\circ{}_{ji}(r)) &= \\ c^\lambda{}_\mu\, q^\mu D_\lambda f^\circ{}_{ji}(r) + \tfrac{1}{2}\, b^\lambda{}_{\mu\nu}\, q^\mu q^\nu D_\lambda f^\circ{}_{ij}(r).\end{aligned}$$

This polynomial may be written in a more convenient form, (which may be verified by substitution of (3.2.6) and using (3.2.4) and the fact that $D_l f(r) = q^l \left(\frac{\mathrm{d}f(r)}{r\,\mathrm{d}r}\right)$, as follows

$$c^{\lambda}{}_{\mu}\, D^2{}_{\lambda\mu}\, \zeta(r) + \tfrac{1}{2}\, b^{\lambda}{}_{\mu\nu} D^3{}_{\lambda\mu\nu}\theta(r) - \tfrac{1}{2}\, b_{\lambda\mu\mu}\, D_{\lambda}\, \zeta(r) \tag{3.2.5}$$

when the functions $\zeta(r)$ and $\theta(r)$ are defined by

$$f^{\circ}{}_{ji}(r) = \frac{d\zeta(r)}{r\,\mathrm{d}r} = \frac{\mathrm{d}^2\theta(r)}{(r\,\mathrm{d}r)^2}. \tag{3.2.6}$$

This device, which will be employed consistently in the following, serves to convert a rather unwieldly polynomial into a sum of derivatives of functions of r alone. In this form, we may consider the various quantities to be functions of r with operator coefficients, which commute agreeably with other partial differentiation operators, such as $\Delta = D^2{}_{\lambda\lambda}$.

3.3. *Transformation of Vector Variables.*

When we recall that the derivation of the equation of continuity involved two terms, one of which referred to the volume element dV_1 and the other to dV_2, it is clear that the final form (2.5.7) will include functions of both $\mathbf{r}_1$ and $\mathbf{r}_2$, as well as $\mathbf{r}_{21}$ and $\mathbf{r}_{12}$ as independent variables. With the help of the relations

$$\mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}_{21} = -\mathbf{r}_{12},$$

we shall transform the terms to functions of $\mathbf{r}_1$ and $\mathbf{r}_{21}$ as independent variables. We have to deal with functions of the type $\varphi(\mathbf{r}_1, \mathbf{r}_{21})$ (or equally well $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$), describing the conditions in the atmosphere of an ion situated at $\mathbf{r}_1(\mathbf{r}_2)$ at the distance $\mathbf{r}_{21}(\mathbf{r}_{12})$ from this ion. The asymmetry of the ionic atmospheres will be proportional to the velocity gradient. We have assumed that the latter varies linearly with location, and we may make the same assumption for the function φ, namely that $\varphi(\mathbf{r}_1, \mathbf{r}_{21})$ is linear in $\mathbf{r}_1$.

Our task is to express a function $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$, (linear in $\mathbf{r}_2$) in the variables $\mathbf{r}_1, \mathbf{r}_{21}$. We introduce an operator "Grad" defined by

$$\mathrm{Grad}^l\varphi = \left\{\left(\frac{\partial}{\partial q^l{}_1}\right)_{\mathbf{r}_2} + \left(\frac{\partial}{\partial q^l{}_2}\right)_{\mathbf{r}_1}\right\}\varphi \tag{3.3.1}$$

which refers to displacement of an ion together with its atmosphere. The transformation of $\varphi(\mathbf{r}_2, \mathbf{r}_{12})$ then becomes

$$\varphi(\mathbf{r}_2, \mathbf{r}_{12}) = \varphi, (\mathbf{r}_1 - \mathbf{r}_{21}) + (\mathbf{r}_{21}, \mathrm{Grad}\, \varphi(\mathbf{r}_1, -\mathbf{r}_{21})). \tag{3.3.2}$$

Obviously

$$\mathrm{Grad}^l\varphi(\mathbf{r}_1, \mathbf{r}_{21}) = \left(\frac{\partial}{\partial q^l{}_1}\varphi(\mathbf{r}_1, \mathbf{r}_{21})\right)_{\mathbf{r}_{21} = \mathrm{const.}}$$

Using (3.3.2) and the fact that

$$\Delta_1\varphi(\mathbf{r}_2, \mathbf{r}_{12}) = \left(\frac{\partial^2\varphi}{\partial q^{\lambda}{}_1\, \partial q^{\lambda}{}_1}\right)_{q_2} = \left(\frac{\partial^2\varphi}{\partial q^{\lambda}{}_{21}\partial q^{\lambda}{}_{21}}\right) = \Delta\varphi,$$

we obtain

$$\Delta_1\psi'{}_i(\mathbf{r}_2, \mathbf{r}_{12}) = \Delta\psi'{}_i(\mathbf{r}_1, -\mathbf{r}_{21}) + (\mathbf{r}_{21}, \mathrm{Grad}\, \Delta\psi'{}_i(\mathbf{r}_1, -\mathbf{r}_{21})). \tag{3.3.3}$$

From the symmetry condition (2.1.6)

$$\Delta_1 f'_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = \Delta_1 f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21})$$

and the identity

$$\Delta_1 \equiv \frac{\partial^2}{\partial q^\lambda{}_1 \partial q^\lambda{}_1} \equiv \left(\mathrm{Grad}^\lambda - \frac{\partial}{\partial q^\lambda{}_2}\right)^2,$$

we find that

$$\begin{aligned}\Delta_1 f_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) &= \Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) + \mathrm{Div\ Grad}\, f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) - 2\frac{\partial^2}{\partial q^\lambda{}_{21} \partial q^\lambda{}_1} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \\ &= \Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) - 2\frac{\partial^2}{\partial q^\lambda{}_{21} \partial q^\lambda{}_1} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}). \qquad (3.3.4)\end{aligned}$$

(we recall that f'_{ji} is a linear function of $\mathbf{r}_1$, annihilated by the operator Div Grad).

3.4 *The Differential Equations for the Potentials.*

If now (3.2.5), (3.3.3) and (3.3.4) are substituted in the equation of continuity (2.5.7), and the external forces $\mathbf{K}_i$ and $\mathbf{K}_j$ are set equal to zero, we obtain the system of s^2 differential equations

$$\begin{aligned}&(c^\lambda{}_\mu D^2{}_{\lambda\mu}\zeta(r) + \tfrac{1}{2}\, b^\lambda{}_{\mu\nu} D^3{}_{\lambda\mu\nu}\theta(r) - \tfrac{1}{2}\, b^\lambda{}_{\mu\mu} D_\lambda \zeta(r)) - e_i\omega_i n_i n_j \Delta\psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) \\ &\quad - e_j\omega_j n_i n_j \Delta\psi'_i(\mathbf{r}_1, -\mathbf{r}_{21}) - (\omega_i + \omega_j)kT\,\Delta f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) \\ &\quad - e_j\omega_j n_i n_j(\mathbf{r}_{21}, \Delta\ \mathrm{Grad}\ \psi'_i) + 2\omega_j kT \frac{\partial^2}{\partial q^\lambda{}_{21}\partial q^\lambda{}_1} f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = 0 \qquad (3.4.1)\end{aligned}$$

which connect the s^2 distribution functions f'_{ji} with the s potentials ψ'_j for the case that a velocity gradient described by (3.2.1) is present in an electrolyte, while there are no external forces acting on the ions. The system (3.4.1) is made complete by means of the s Poisson equations (2.5.3).

The functions ψ'_j and f'_{ji} which give the deviations of potential and distribution from their values $\psi^\circ{}_j$ and $f^\circ{}_{ji}$ characteristic of the solution at rest, depend on distance and direction between pairs of ions and hence may be expanded in the form

$$\sum_n A_n\, q^\lambda \ldots q^\mu\, g_n(r),$$

or preferably in the more convenient form (compare with 3.2.5)

$$\sum_n B_n\, D^n{}_{\lambda \ldots \mu}\, h_n(r).$$

The original assumption of a linear velocity gradient leads to three types of terms in the known function of r (3.2.5) which appears in (3.4.1) and therefore to the same approximation, we may set

$$\begin{aligned}\psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) &= b^\lambda{}_{\mu\mu} D_\lambda v_j(r) + c^\mu{}_\nu D^2{}_{\mu\nu}\xi_j(r) + \tfrac{1}{2}\, b^\lambda{}_{\mu\nu} D^3{}_{\lambda\mu\nu} u_j(r) \\ f'_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) &= b^\lambda{}_{\mu\mu} D_\lambda G_{ji}(r) + c^\mu{}_\nu D^2{}_{\mu\nu}\varphi_{ji}(r) + \tfrac{1}{2}\, b^\lambda{}_{\mu\nu} D^3{}_{\lambda\mu\nu} F_{ji}(r) \\ \psi'_i\,(\mathbf{r}_1, -\mathbf{r}_{21}) &= -b^\lambda{}_{\mu\mu} D_\lambda v_i(r) + c^\mu{}_\nu D^2{}_{\mu\nu}\xi_i(r) - \tfrac{1}{2}\, b^\lambda{}_{\mu\nu} D^3{}_{\lambda\mu\nu} u_i(r). \qquad (3.4.2)\end{aligned}$$

(In $\psi'_i(\mathbf{r}_1, -\mathbf{r}_{21})$, the odd terms obtain the sign minus because the differentiations indicated by D are with respect to the components of $+\mathbf{r}_{21}$). Substitution of (3.4.2) in (3.4.1) gives an equation of the form

$$b^{\lambda}{}_{\mu\mu}D_{\lambda}L_1\left\{U_1(r)\right\} + c^{\mu}{}_{\nu}D^2{}_{\mu\nu}L_2\left\{U_2(r)\right\} + b^{\lambda}{}_{\mu\nu}D^3{}_{\lambda\mu\nu}L_3\left\{U_3(r)\right\} = 0 \quad (3.4.3)$$

(since the order of partial differentiation is immaterial), where the L's represent symbolically the three parts of the resulting equation. This is equivalent to three equations

$$b^{\lambda}{}_{\mu\mu}D_{\lambda}\, L_1\left\{U_1(r)\right\} = 0 \quad (3.4.4)$$

$$c^{\lambda}{}_{\mu}\, D^2{}_{\mu\nu}\, L_2\left\{U_2(r)\right\} = 0 \quad (3.4.5)$$

$$b^{\lambda}{}_{\mu\nu}\, D^3{}_{\lambda\mu\nu}\, L_3\left\{U_3(r)\right\} = 0, \quad (3.4.6)$$

for (3.4.3), a polynomial in the coordinates, can vanish only if the coefficients vanish separately.

Now the stress $S^*{}_{lm}$ is to be computed as an average sum of the forces between ions and it will be seen that the averaging process will eliminate terms of the sum involving odd powers of the coordinates. Consequently we shall need to compute only the even part $c^{\mu}{}_{\nu}D^2{}_{\mu\nu}\xi_j(r)$ of the potential in order to evaluate the stress and shall require the odd terms only for the special consideration of the mechanism of force transfer. (Appendix II). Our immediate problem then is the solution of

$$c^{\mu}{}_{\nu}D^2{}_{\mu\nu}L_2\left\{U_2(r)\right\} = 0.$$

Since $L_2\left\{U_2(r)\right\}$ is a function $R(r)$ of r, this is equivalent to

$$c^{\mu}{}_{\nu}D^2{}_{\mu\nu}q^{\mu}q^{\nu}\frac{d^2R(r)}{(r\,dr)^2} = 0,$$

(because by (3.2.4), $c^{\mu}{}_{\mu} = c^{\nu}{}_{\nu} = 0$), and has the solution

$$R(r) = A_1r^2 + A_2, \quad (3.4.7)$$

where A_1 and A_2 are constants to be determined by the boundary condition that the potential must vanish for r large. We substitute (3.4.3) in (3.4.1), select the even terms, and obtain

$$c^{\mu}{}_{\nu}D^2{}_{\mu\nu}\left\{\zeta(r) - e_i\omega_in_in_j\,\Delta\xi_j - e_j\omega_jn_in_j\Delta\xi_i - (\omega_i + \omega_j)kT\Delta\varphi_{ji}\right\} = 0 \quad (3.4.8)$$

(the last two terms of (3.4.1) contain only odd functions of the coordinates).

The distribution function $\Delta\varphi_{ji}$ is eliminated from (3.4.8) by means of the relation

$$c^{\mu}{}_{\nu}\, D^2{}_{\mu\nu}\left(\Delta\xi_j + \frac{4\pi}{D}\sum_i\frac{e_i}{n_j}\,\varphi_{ji}\right) = 0 \quad (3.4.9)$$

obtained by substituting (3.4.2) in the Poisson equation and selecting the even part. This elimination gives us s equations to determine the even part of the s potentials ψ'_j, namely $c^{\mu}{}_{\nu}D^2{}_{\mu\nu}\ \xi_j(r)$, as follows:

$$c^{\mu}{}_{\nu}D^2{}_{\mu\cdot}\left(\Delta\Delta\xi_j - \frac{4\pi}{DkT}\sum_i\frac{n_ie^2{}_i\omega_i}{\omega_i + \omega_j}\Delta\xi_j - \frac{4\pi}{DkT}\sum_i\frac{e_ie_j\omega_jn_i}{\omega_i + \omega_j}\Delta\xi_i\right.$$
$$\left. + \frac{4\pi}{DkT}\sum_i\frac{e_i}{n_j}\frac{\zeta(r)}{\omega_i + \omega_j}\right) = 0. \quad (3.4.10)$$

Recalling the definition (3.2.6) of $\zeta(r)$

$$\frac{d\zeta(r)}{r\,dr} = n_j n_i\left(1 - \frac{e_j e_i}{DkT}\,\frac{e^{-\kappa r}}{r}\right),$$

$\zeta(r)$ is found by integration to be

$$\zeta(r) = \frac{e_j e_i n_j n_i}{\kappa DkT} e^{-\kappa r} + \frac{n_j n_i}{2} r^2 + C_1.$$

This is substituted in (3.4.10), the integration (3.4.7) is performed and the constants A_1 and A_2 are chosen to eliminate the last two terms of $\zeta(r)$, as required by the boundary conditions. Thus we obtain in the final form the equations which determine $\xi_j(r)$:

$$\Delta\Delta\xi_j - \frac{4\pi}{DkT}\sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j}\Delta\xi_j - \frac{4\pi}{DkT}\sum_i \frac{e_i e_j \omega_j n_i}{\omega_i + \omega_j}\Delta\xi_i$$

$$= -\frac{4\pi}{(DkT)^2}\,\frac{e^{-\kappa r}}{\kappa}\sum_i \frac{n_i e_i^2\, e_j}{\omega_i + \omega_j}. \qquad (3.4.11)$$

3.5. *Matrix Formation and Solution.*

The s equations (3.4.11) which determine the even parts of the potentials ψ'_j of the distorted ionic atmospheres can be dealt with most conveniently with the aid of the theory of quadratic forms. We shall first write (3.4.11) in a more compact form by the use of the following notation:

$$a_{ji} = \left(\delta_{ji}\sum_{k=1}^{s} \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j}\right)\frac{4\pi}{DkT} \qquad (3.5.1)$$

$$t_j = \frac{-4\pi}{(DkT)^2\kappa}\sum_{i=1}^{s} \frac{n_i e_i^2}{\omega_i + \omega_j}\, e_j, \qquad (3.5.2)$$

where δ_{ji} is the well known Kronecker symbol

$$\delta_{ji} = \begin{cases} 1, \text{ if } j = i \\ 0 \text{ if } j \neq i. \end{cases}$$

In this notation, (3.4.11) becomes

$$\sum_{i=1}^{s} \Delta(\Delta\delta_{ji} - a_{ji})\,\xi_i = t_j e^{-\kappa r} \qquad (3.5.3)$$

or, using the convention that Greek indices imply summation (here, of course, from 1 to s),

$$\Delta(\Delta\delta_{j\sigma} - a_{j\sigma})\,\xi_\sigma = t_j e^{-\kappa r}. \qquad (3.5.4)$$

If we now introduce a space of s dimensions, t_j may be considered as the j-th component of a vector $\mathbf{t}$ in this space, and a_{ji} as the i-th element of the j-th row of a matrix A or the corresponding element of the tensor operator $\mathbf{A}$. Also δ_{ji} is the general component of the unit matrix E

$$E = \begin{pmatrix} 1 & 0 & . & . & . & 0 \\ 0 & 1 & . & . & . & 0 \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & 1 \end{pmatrix} = (\delta_{ji})$$

corresponding to the unit tensor $\mathbf{E} = 1$.
Then (3.5.4) may be interpreted as a linear operation

$$\Delta(\Delta - \mathbf{A})\,\mathbf{x} = \mathbf{t}\,e^{-\kappa r} \tag{3.5.5}$$

where $\Delta(\Delta - \mathbf{A})$ acting on an unknown vector $\mathbf{x}$ (which is a function of r) produces a known vector $\mathbf{t}$ multiplied by the known scalar function $\exp(^{-\kappa r})$.

We shall show later in discussing the matrix A, that its "characteristic numbers" $\alpha_1, \alpha_2, \ldots, \alpha_s$ are all positive. That being the case, it is possible to find matrices B, such that

$$B^2 = A : b_{j\lambda}\, b_{\lambda i} = a_{ji} \tag{3.5.6}$$

and a matrix B with this property will be real. The equation (3.5.6) has actually several (in general 2^s) solutions B, with the characteristic numbers $\pm\sqrt{\alpha_1}, \ldots \pm\sqrt{\alpha_s}$. Among these solutions we shall select the one that has only positive characteristic numbers $+\sqrt{\alpha_1}, \ldots +\sqrt{\alpha_s}$, and designate it simply as B.

Now if $\chi(r, \beta)$ is the solution of

$$\Delta(\Delta - \beta^2)\, \chi(r, \beta) = e^{-\kappa r} \tag{3.5.7a}$$

then[1]

$$\Delta(\Delta - \mathbf{B}^2)\chi(r, \mathbf{B}) = e^{-\kappa r}\, \mathbf{1}, \tag{3.5.7b}$$

so that $\Delta(\Delta - \mathbf{B}^2)\, \chi(r, \mathbf{B})$ operating on $\mathbf{t}$ is equivalent to multiplying $\mathbf{t}$ by the scalar $e^{-\kappa r}$; that is,

$$\mathbf{x} = \chi(r, \mathbf{B})\, \mathbf{t} \tag{3.5.8}$$

is the solution of (3.5.5). We therefore investigate the solution of (3.5.7a).

A particular solution is

$$\chi(r, \beta) = \frac{\partial}{\partial\kappa}\left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)}\,\frac{e^{-\kappa r}}{r}\right),$$

to which must be added the general solution of the homogeneous equation, giving as the complete solution

$$\chi(r, \beta) = \frac{\partial}{\partial\kappa}\left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)}\,\frac{e^{-\kappa r}}{r}\right) + A_1\frac{e^{-\beta r}}{r} + A_2\frac{1}{r} + A_3\frac{e^{\beta r}}{r} + A_4\, r^2. \tag{3.5.9}$$

---

[1] A polynomial function $P(\mathbf{B})$ is defined as

$$\sum_{\nu=1}^{n} a_\nu \mathbf{B}^\nu \qquad \text{if } P(\beta) = \sum_{\nu=1}^{n} a_\nu\, \beta^\nu.$$

The reciprocal $(\chi(\mathbf{B}))^{-1}$ of a function $\chi(\mathbf{B})$ is defined by $\chi(\mathbf{B})\,(\chi(\mathbf{B}))^{-1} = 1$ (assuming that $\chi(\mathbf{B})$ is not a degenerate matrix, that is, its determinant $|\chi(\mathbf{B})|$ must not vanish.) An n-th root $\mathbf{A}^{1/n}$, which is, of course, multiple-valued, is defined by $(\mathbf{A}^{1/n})^n = \mathbf{A}$. A transcendental function may defined by its power series if it converges, which is certainly the case for an *entire* function, e.g. the exponential function. This list includes all the functions of matrices that we shall need.

The constants $A_1 \ldots A_4$ must be evaluated by the boundary conditions of our problem. Let us assume for a moment, in analogy with (3.4.2), that

$$c^\lambda{}_\mu\, D^2{}_{\lambda\mu}\chi(r, \beta) \equiv O_2\,\{\chi(r, \beta)\} = c^1{}_1 \frac{\partial^2\chi}{\partial x^2} + 2\, c^1{}_2 \frac{\partial^2\chi}{\partial x\partial y} + \ldots + c^3{}_3 \frac{\partial^2\chi}{\partial z^2}$$

where $c^\lambda{}_\lambda = c^1{}_1 + c^2{}_2 + c^3{}_3$ (cf. (3.2.4)), describes the potential in the neighborhood of an ion (except for a constant factor, corresponding to **t** in (3.5.5)). Then the following boundary conditions must hold: For $r = \infty$, $O_2\{\chi\}$ must vanish, or the ion would make its presence felt at infinite distance. For $r = 0$, we must require that the power series for $\chi(r)$ and for $\Delta\chi(r)$ contain no negative powers of r: A term $(1/r)$ in the expansion of $\chi(r)$ would lead to a singularity $O_2\{1/r\} = c^\lambda{}_\mu\, D^2{}_{\lambda\mu}(1/r)$ in the potential $O_2(\chi)$. According to potential theory such a singularity represents a quadrupole at $r = 0$, which is inadmissible. A term $(1/r)$ in $\Delta\chi$ must be excluded because $\Delta(O_2\{\chi\}) = O_2\{\Delta\chi\}$ is proportional to the charge density and

$$O_2\{1/r\} = c^\lambda{}_\mu q^\mu q^\nu \frac{1}{r^5}$$

is not even integrable near $r = 0$, and would imply an infinite charge present in a finite volume.

The boundary condition for $r = \infty$ then requires

$$A_3 = A_4 = 0.$$

The power series for $\chi(r, \beta)$ starts with the term

$$\left(\frac{\partial}{\partial\kappa}\left(\frac{1}{\kappa^2(\beta^2 - \kappa^2)}\right) + A_1 + A_2\right)\frac{1}{r}$$

and the series for $\Delta\chi$ with

$$\left(\frac{\partial}{\partial\kappa}\left(\frac{1}{\beta^2 - \kappa^2}\right) + A_1\beta^2\right)\frac{1}{r}$$

and there are no other negative powers of r to be considered. The necessary and sufficient requirements for fulfilling our boundary conditions are therefore:

$$A_1 = \frac{\partial}{\partial\kappa}\left(\frac{-1}{\beta^2(\beta^2 - \kappa^2)}\right)$$

$$A_2 = \frac{\partial}{\partial\kappa}\left(\frac{-1}{\beta^2\kappa^2}\right).$$

Inserting these values in (3.5.9) we obtain

$$\chi(r, \beta) = \frac{\partial}{\partial\kappa}\left(\frac{\beta^2 e^{-\kappa r} - \kappa^2 e^{-\beta r} - (\beta^2 - \kappa^2)}{\beta^2\kappa^2(\beta^2 - \kappa^2)r}\right). \qquad (3.5.10)$$

This solution holds for all positive values of β. In order to cover the special case $\beta = \kappa$, we need only point out that the factor $(\beta - \kappa)$ in the denominator is really harmless, because it can be divided out from the expanded power series of the numerator.

Now consider

$$\chi(r, \mathbf{B}) = \frac{1}{r}\frac{\partial}{\partial\kappa}(\kappa^{-2}(\mathbf{B}^2 - \kappa^2)^{-1}\, e^{-\kappa r} - \mathbf{B}^{-2}(\mathbf{B}^2 - \kappa^2)^{-1} \exp(-\mathbf{B}r) - \kappa^{-2}\mathbf{B}^{-2})$$

which, since the presence of only one matrix or functions thereof does not affect the rules of algebra[1] will be a (particular) solution of (3.5.7b), as (3.5.10) is a solution of (3.5.7a). Furthermore,

$$\mathbf{x}(r) = \chi(r, \mathbf{B})\,\mathbf{t}$$

is a particular solution of (3.5.5).

Since we have already adjusted the arbitrary constants in $\chi(r, \beta)$ to satisfy the boundary conditions for a potential, we may expect that the components $\xi_1, \ldots \xi_s$ of $\mathbf{x}$, (or rather $c^\lambda{}_\mu D_{\lambda\mu}\xi_1$, etc.) will be equally agreeable. Indeed, we have chosen all the characteristic values of B positive, so that $\exp(-\mathbf{B}r)$ will vanish for $r = \infty$ and the same applies to all components of $(\exp(-\mathbf{B}r), \mathbf{t})$. It is fairly obvious that the other terms in $\chi(r, \mathbf{B})$ vanish for $r = \infty$. As regards the boundary conditions for $r = 0$, we have shown already that $\chi(r, \beta)$ and $\Delta\chi(r, \beta)$ contain no negative powers of r; similarly, neither $\chi(r, \mathbf{B})$ nor $\Delta\chi(r, \mathbf{B})$ will contain negative powers of r. The same, then, applies to $\xi_j(r)$ and $\Delta\xi_j(r)$, which are the j- components of

$$\mathbf{x} = (\chi(r, \mathbf{B}), \mathbf{t}) \tag{3.5.11}$$

and

$$\Delta\mathbf{x} = (\Delta\chi(r, \mathbf{B}), \mathbf{t}) \tag{3.5.12}$$

respectively. Thus (3.5.11) is a solution of (3.5.5), satisfying the appropriate boundary conditions. It remains to demonstrate that this solution is unique. For that purpose we consider the most general solution of the homogeneous equation

$$\Delta(\Delta - \mathbf{B}^2)\,\mathbf{x}^* = 0,$$

which is

$$\mathbf{x}^* = \frac{1}{r}\Big(\exp(-\mathbf{B}r), \mathbf{a}\Big) + \frac{1}{r}\mathbf{b} + \frac{1}{r}\Big(\exp \mathbf{B}r, \mathbf{c}\Big) + r^2\mathbf{d}$$

where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$ are arbitrary vectors. If we could find vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, $\mathbf{d}$ (not all zero) such that (every component of) $\mathbf{x}^*$ would satisfy the above boundary conditions ($\mathbf{x}^*$ and $\Delta\mathbf{x}^*$ free from singularities for $r = 0$, $\mathbf{x}^* \rightarrow 0$ for $r \rightarrow \infty$), we might add $\mathbf{x}^*$ to (3.5.11). That, however, is not the case, so that (3.5.11) is unique. Written in components, (3.5.11) takes the form

$$\xi_j(r) = \chi(r, B)_{j\sigma} t_\sigma. \tag{3.5.13}$$

It will turn out that we shall need only the value of $\Delta\xi_j$ for $r = 0$ in order to compute the stress $S^*{}_{mn}$; we shall therefore anticipate somewhat by evaluating $\Delta\xi_j(0)$ at this point. By differentiating (3.5.10), we obtain

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[1] It takes two matrices to form a non-commutative product.

$$\Delta\chi(r, \beta) = \frac{\partial}{\partial\kappa}\left(\frac{e^{-\kappa r} - e^{-\beta r}}{r(\beta^2 - \kappa^2)}\right) \tag{3.5.14}$$

and

$$\Delta\chi(0, \beta) = \lim_{r\to 0}\frac{\partial}{\partial\kappa}\left(\frac{(1-\kappa r+\frac{1}{2}\kappa^2r^2+\ldots)-(1-\beta r+\frac{1}{2}\beta^2r^2+\ldots)+\ldots}{r(\beta+\kappa)\,(\beta-\kappa)}\right)$$

$$= \frac{\partial}{\partial\kappa}\left(\frac{1}{\beta+\kappa}\right) = \frac{-1}{(\beta+\kappa)^2}. \tag{3.5.15}$$

Similarly

$$\Delta\xi_j(0) = -(B + \kappa)^{-2}{}_{j\sigma}\, t_\sigma. \tag{3.5.16}$$

3.6. *Calculation of Stress.*

In accordance with our preliminary consideration in §3.1, we imagine the electrolyte confined between two plates, (Fig. 2), one of which moves in the x-direction, and investigate the total transport of electrostatic force AS^*_{yx} across an area A of a plane $y = y_0$ in the x-direction, assuming a velocity gradient with only one component

$$\frac{\partial v_x}{\partial y} = a'_2.$$

The Coulomb force between any two ions is

$$\frac{e_je_i}{D}\frac{\mathbf{r}_{21}}{r^3},$$

where $\mathbf{r}_{21}$ is the vector which locates the second ion with respect to the first. Now if a pair of ions is to contribute anything to AS^*_{yx}, the stress *across* the plane, they must obviously be on opposite sides of the plane $y = y_0$, so that we must consider only pairs of ions whose coordinates satisfy the restriction

$$y_1 < y_0 < y_2$$

if $\mathbf{r}_1$ locates the first ion and $\mathbf{r}_2$ the second. Let us now calculate the mutual forces between the ions in two volume elements dV_1 and dV_2 located on opposite sides of the plane. The force transferred from a j-ion in dV_1 to the ions in dV_2 is

$$\frac{e_j}{D}\sum_i e_in_{ji}(\mathbf{r}_{21})\,\mathrm{d}V_2\frac{\mathbf{r}_{21}}{r^3}.$$

The total interaction between all pairs of ions in the two volume elements is then:

$$\sum_j\frac{n_je_j}{D}\,\mathrm{d}V_1\sum_i e_in_{ji}(\mathbf{r}_{21})\,\mathrm{d}V_2\frac{\mathbf{r}_{21}}{r^3} = \sum_{ji}\frac{e_je_i}{D}f_{ji}(\mathbf{r}_{21})\mathrm{d}V_1\mathrm{d}V_2\frac{\mathbf{r}_{21}}{r^3}$$

$$= -\sum_{ji}\frac{e_ie_j}{D}f_{ij}(\mathbf{r}_{12})\,\mathrm{d}V_1\mathrm{d}V_2\frac{\mathbf{r}_{12}}{r^3}.$$

The total transfer of force across a plane $y = y_0$ is obtained by integrating over all volume elements satisfying the condition $y_1 < y_0 < y_2$. Thus, if the area of the plane $y = y_0$ be $A = \int \mathrm{d}z\,\mathrm{d}x$, the x component of the force transferred across this plane equals[1]

$$-AS^*_{yx} = \underset{y_1 < y_0 < y_2}{\int\int\int\int\int\int} \sum \frac{e_i e_j}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21}}{r^3} \mathrm{d}V_1\,\mathrm{d}V_2$$

$$= \underset{\substack{y_{21} > 0 \\ y_0 - y_{21} < y_1 < y_0}}{\int\int\int\int\int\int} \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21}}{r^3} \mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}z_1\,\mathrm{d}V_{21}. \qquad (3.6.1)$$

Integration over x_1 and z_1 yields a factor A; integration over y_1 a factor y_{21}. Thus

$$-S^*_{yx} = \underset{y_{21} > 0}{\int\int\int} \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r}_{21}) \frac{x_{21} y_{21}}{r^3} \mathrm{d}V_{21}$$

or, since we may now drop the indices 21 without causing confusion

$$-S^*_{yx} = \underset{+y > 0}{\int\int\int} \frac{xy}{r^3} \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r})\,\mathrm{d}V.$$

We may extend the region of integration to the whole space by utilizing the identity $f_{ji}(\mathbf{r}) = f_{ij}(-\mathbf{r})$ whence, interchanging indices of summation

$$\frac{xy}{r^3} \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r}) = \frac{(-x)\,(-y)}{r^3} \sum_{ij} \frac{e_i e_j}{D} f_{ij}(-\mathbf{r}).$$

Introducing the arithmetic mean of right and left-hand members of this into (3.6.1), we obtain

$$S^*_{yx} = -\frac{1}{2} \int\int\limits_{-\infty}^{+\infty}\int \frac{xy}{r^3} \sum_{ji} \frac{e_j e_i}{D} f_{ji}(\mathbf{r})\,\mathrm{dV}.$$

By means of the Poisson equation (2.5.3), the potential sum $\sum\limits_j \psi_j$ is substituted:

$$S^*_{yx} = \frac{1}{8\pi} \int\int\limits_{-\infty}^{+\infty}\int \sum_j n_j e_j \Delta\psi_j(\mathbf{r}_{21}) \frac{xy}{r^3}\,\mathrm{d}V.$$

We shall now compute this integral. Since $\psi_j(\mathbf{r}_{21}) = \psi^\circ_j(r) + \psi'_j(\mathbf{r}_{21})$, the contribution to the integral of the potential $\psi^\circ_j(r)$ characteristic of the undisturbed state will be nil since $\Delta\psi_j$ is multiplied by xy. Likewise, the terms of ψ'_j which are odd in the coordinates will average out, so that the integral reduces to

$$S^*_{yx} = \frac{1}{8\pi} \int\int\limits_{-\infty}^{+\infty}\int \sum_j n_j e_j (a^\lambda{}_\mu D^2{}_{\lambda\mu} \Delta\xi_j(r)) \frac{xy}{r^3}\,\mathrm{d}V$$

in view of the definition of ξ_j in (3.4.2) and of d_m in (3.2.2).

---

[1] We use the customary sign convention that pressures are reckoned negative and tensions positive. Here we clearly have to do with a pressure: the Coulomb law as written is positive for a repulsive force.

For the special case under consideration, namely, $a^1{}_2 = a^1{}_2$, $a^l_m = 0$ otherwise, we obtain

$$S^*_{yx} = \frac{1}{8\pi}\int\int_{-\infty}^{+\infty}\int \sum_j n_j e_j \frac{xy}{r^3} a^1{}_2 \frac{\partial^2}{\partial x\,\partial y} \Delta\xi_j\,(r)\,\mathrm{d}V$$

$$= \frac{a^1{}_2}{8\pi}\sum_j n_j e_j \int\int_{-\infty}^{\infty}\int \frac{x^2y^2}{r^3}\,\frac{\mathrm{d}^2\Delta\xi_j(r)}{(r\,\mathrm{d}r)^2}\,\mathrm{dV}$$

or in polar coordinates,

$$S^*_{yx} = \frac{a^1{}_2}{8\pi}\sum_j n_j e_j \int_0^\infty\int_0^{2\pi}\int_0^\pi r^3 \sin^3\theta \cos^2\theta \sin^2\varphi\,\frac{\mathrm{d}^2\Delta\xi_j(r)}{(r\,\mathrm{d}r)^2}\,\mathrm{d}r\,\mathrm{d}\varphi\,\mathrm{d}\theta.$$

$$= \frac{a^1{}_2}{30}\sum_j n_j e_j \int_0^\infty \frac{\mathrm{d}^2\Delta\xi_j(r)}{(r\,\mathrm{d}r)^2}\,r^3\,\mathrm{d}r.$$

Integrating twice by parts,

$$S^*_{yx} = \frac{a^1{}_2}{15}\sum_j n_j e_j \Delta\xi_j(0).$$

Here we substitute the values of $\Delta\xi_j(0)$ obtained in (3.5.16)

$$S^*_{yx} = -\frac{a^1{}_2}{15}\sum_j n_j e_j (B+\kappa)^{-2}{}_{j\sigma} t_\sigma$$

whence, by comparison with (3.1.4)

$$\eta^* = -\frac{1}{15}\sum_{ji} n_j e_j (B+\kappa)^{-2}{}_{ji} t_i \tag{3.6.2}$$

for the electrostatic contribution in viscosity.

In vector notation for convenient manipulation,

$$\eta^* = -\frac{1}{15}\mathbf{u}\,(\mathbf{B}+\kappa)^{-2}\,\mathbf{t} \tag{3.6.3}$$

where **u** is a vector with components $n_j e_j$.

3.7. *Final Formula for Viscosity.*

The mathematical details of the computation of the product (3.6.3) in the viscosity η^* have been relegated to Appendix I, in order that the continuity of the physical considerations should not be broken. Here we shall present and discuss only the results.

For the general case of a solution containing s species of ions, the electrostatic contribution to the viscosity is

$$\eta^* = \frac{1}{120\,\kappa DkT}\left(\sum_i \frac{n_i e_i^2}{\omega_i} - 4\,\mathbf{p}\sum_{n=0}^{\infty} c_n\,\mathbf{q}^{(n)}\right) \tag{3.7.1}$$

$$= 0.362\left(\frac{\Gamma}{DT}\right)^{1/2}\left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4\,\mathbf{r}\sum_{n=0}^{\infty} c_n\,\mathbf{s}^{(n)}\right) \tag{3.7.2}$$

where c_n, μ_i, $\mathbf{r}$, $\mathbf{s}^{(o)}$ and $\mathbf{s}^{(n)}$ are given by (3.8.25), (3.8.32), (3.8.42), (3.8.43), and (3.8.45), respectively. The second form is more convenient for practical calculations; $\Gamma_i = \sum_i \Gamma_i = \sum_j m_i z_i^2$ is total ionic strength (3.8.31), z_i is valence, m_i is concentration in mols per liter and Λ_i is equivalent conductance measured in ordinary units (ohm^{-1} cm^2 per equiv.). The second term in the brackets is a correction term involving the second power of the difference in mobilities of various ions; formulas for its exact computation are given in the appendix (3.8.27) and (3.8.44). The first term, proportional to an average fractional coefficient

$$\bar{\rho} = (\sum_i n_i e_i^2 \rho_i)/(\sum_i n_i e_i^2)$$

is dominant except when the ρ's exhibit great (relative) differences. This observation, first made by Falkenhagen for the simple electrolyte, is hereby extended to the general case. In (3.7.2), the terms in the brackets do not contain the concentrations except as ratios; the whole effect is therefore *proportional to the square root of the concentration* for a given mixture of ions. In this regard, then, we again corroborate Falkenhagen's result for a simple electrolyte.

When $\omega_1 = \omega_2 = \ldots = \omega_s = \omega$, the correction term vanishes, and we obtain

$$\eta^* = \frac{\kappa}{480\pi\omega} \tag{3.7.3}$$

which, except for a factor of 60 is the result of our preliminary calculations in §3.1. This result may be given an interesting form by substituting the Stokes formula for the coefficient of friction of a spherical particle:

$$\rho = 6\pi\eta r$$

where r is the apparent radius of the ion.
Then

$$\frac{\eta^*}{\eta} = \frac{\kappa r}{0} = \frac{\eta - \eta^\circ}{\eta}, \tag{3.7.4}$$

which shows that in the first approximation the relative change in viscosity is proportional to the ratio between the radius of an ion and that of its atmosphere.

The case of two ions having materially different mobilities has been discussed by Falkenhagen. We have calculated numerically one example of a mixture containing 3 ions, namely H^+, K^+ and Cl^- in water at 25° (Λ = 349.7, 73.5, 76.3, respectively). Fig. 3 gives η^* as a function of μ_1, the ratio of H^+ concentration to *total* ion concentration ($H^+ + K^+ + Cl^-$), the latter constant at 0.2 normal. For comparison, $\eta^\circ = 8950 \times 10^{-6}$.

3.8. *Appendix I.* Discussion of Matrices.

a) *Characteristic Numbers and Vectors.*

We must now consider the properties of the matrices A and B and, in particular, convert the operator $(\mathbf{B} + \kappa)^{-2}$ into a convenient form for manipulation. The final result for the latter step will give the viscosity as an explicit term in ionic strengths and mobilities, plus a correction term which will depend on the *square* of the *difference* in mobilities of the various ions present. In order to discuss the matrix A conveniently, we shall first transform it into a symmetrical matrix K: if we then consider the elements k_{ji} of the latter as the coefficients of a quadratic form $K(x, x)$, we may apply the well-known theory[1] of orthogonal transformations of quadratic forms.

The general element of A (3.5.1) was defined as

$$a_{ji} = \frac{4\pi}{DkT}\left(\delta_{ji}\sum_k \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j}\right).$$

By means of the transformation

$$\begin{aligned} K &= RAR^{-1}, \ (A = R^{-1}KR) \\ r_{ji} &= \delta_{ji}\sqrt{n_j/\omega_j} \end{aligned} \tag{3.8.1}$$

we obtain the symmetrical matrix K with

$$k_{ji} = k_{ij} = \sqrt{a_{ji}a_{ij}} = \frac{4\pi}{DkT}\left(\delta_{ij}\sum_k \frac{n_k e_k^2 \omega_k}{\omega_k + \omega_j} + \frac{e_i e_j \sqrt{n_i n_j \omega_i \omega_j}}{\omega_i + \omega_j}\right) \tag{3.8.2}$$

The theory of quadratic forms assures that K may be transformed to a diagonal matrix D by means of the linear orthogonal operator[2] L

$$D = LKL' = LRAR^{-1}L' \tag{3.8.3}$$

where the transformation $LR = T$ exists and the result D of the operation (3.8.3) is unique. Then, since the properties of a (symmetrical) matrix are best discussed by considering the diagonal matrix obtained from it by an orthogonal transformation, we shall investigate the elements of D, i.e. the characteristic numbers $\alpha_1, \alpha_2, \ldots, \alpha_s$.

We first prove that K is positive definite and hence that all the characteristic numbers $\alpha_1, \ldots, \alpha_s$ are positive (whereby our previous assertion that A

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[1] The first chapter of Courant & Hilbert's Mathematische Physik contains in compact form all the theory we shall require. Excellent, less compressed presentations are found in A. March: "Die Grundlagen der Quantenmechanik," Chapter IV (1931), and E. Wigner: "Gruppentheorie," Chapters I-III (1931).

[2] A diagonal matrix has all elements zero except those on the diagonal. The operator L satisfies the following conditions (cf. Courant and Hilbert):

$$\begin{aligned} &L\,L' = L'\,L = E \text{ or } L' = L^{-1} \\ &\text{i.e., } l_{p\sigma}l_{q\sigma} = \delta_{pq} \text{ and } l_{\sigma p}l_{\sigma q} = \delta_{pq}. \end{aligned} \tag{3.8.3b}$$

It converts the quadratic form $K(x,x) = k_{\sigma\tau}x_\sigma x_\tau$ into a sum of squares $K(x,x) = \alpha_\sigma y_\sigma y_\sigma$ by the linear transformation

$$x_i = l_{i\sigma}y_\sigma$$

of the variables x_i. The coefficients α_j are called the characteristic numbers of the matrix K and are the diagonal elements of $D = (\delta_{ji}\alpha_{ji})$. They may be found as the roots of

$$\begin{vmatrix} k_{11} - \alpha & k_{12} & . & . & . & k_{1s} \\ k_{21} & k_{22} - \alpha & . & . & . & k_{2s} \\ . & . & . & . & . & . \\ k_{s1} & k_{s2} & . & . & . & k_{ss} - \alpha \end{vmatrix} = 0$$

has real square roots, one of which (B) has only positive characteristic numbers, is justified). The quadratic form corresponding to K is

$$\frac{DkT}{4\pi} K(x, x) = \sum_{jk} \frac{n_k e_k^2 \omega^2_k}{\omega_k + \omega_j} x_j^2 + \sum_{ji} \frac{\sqrt{n_i n_j \omega_i \omega_j}\, e_i e_j x_i x_j}{\omega_i + \omega_j}$$

which by renaming the index k of the double summation may be written

$$\frac{DkT}{4\pi} K(x, x) = \sum_{ji} \frac{n_i e_i^2 \omega_i x_j^2 + \sqrt{n_j \omega_j} e_j \sqrt{n_i \omega_i}\, e_i x_j x_i}{\omega_i + \omega_j}$$

A rearrangement of terms permitted by the double summation leads to

$$\begin{aligned}\frac{DkT}{4\pi} K(x, x) &= \sum_{ij} \frac{n_j e_j^2 \omega_j x_i^2 + 2\sqrt{n_j \omega_j}\, e_j \sqrt{n_i \omega_i}\, e_i x_j x_i + n_i e_i^2 \omega_i x_j^2}{2(\omega_i + \omega_j)} \\ &= \sum_{ij} \frac{(\sqrt{n_j \omega_j}\, e_j x_i + \sqrt{n_i \omega_i}\, e_i x_j)^2}{2(\omega_i + \omega_j)} \\ &\geqslant \sum_{j} \frac{(2\sqrt{n_j \omega_j}\, e_j x_j)^2}{4\omega_j} \\ &> 0 \text{ always.}\end{aligned}$$

Thus $K(x, x)$ is positive definite and its characteristic numbers satisfy

$$\alpha_1 \geqslant \alpha_2 \geqslant \ldots . \geqslant \alpha_s > 0. \qquad (3.8.4)$$

We next prove that

$$\kappa^2 = \frac{4\pi}{DkT} \sum_i n_i e_i^2 \qquad (3.8.4b)$$

is a characteristic number, and, in fact, is greater than any of the others.

$$\begin{aligned}\frac{DkT}{4\pi}\Big(K(x, x) - \kappa^2 E(x, x)\Big) &= \sum_{jk} \frac{n_k e_k^2 \omega_k}{\omega_j + \omega_k} x_j^2 + \\ &\sum_{ji} \frac{\sqrt{n_j n_i \omega_j \omega_i}\, e_i e_j x_j x_i}{\omega_i + \omega_j} - \sum_{ji} n_i e_i^2 x_j^2 \\ &= -\sum_{ji} \frac{\sqrt{n_i \omega_j}\, e_i x_j - \sqrt{n_j \omega_i}\, e_j x_i)^2}{2(\omega_j + \omega_i)} \\ &\leqslant 0\end{aligned}$$

is never positive and is at most zero, which can occur only when

$$\begin{aligned}\frac{x_j}{e_j \sqrt{n_j/\omega_j}} &= \frac{x_i}{e_i \sqrt{n_i/\omega_i}} \\ x_j = l_{1j} &= \frac{e_j \sqrt{n_j \omega_j}}{(\sum_i n_i e_i^2/\omega_i)^{1/2}}\end{aligned} \qquad (3.8.5)$$

giving the normalized eigenvector[1] $\mathbf{l}_1$ corresponding to the characteristic value $\alpha_1 = \kappa^2$.

Thus we have shown that among the characteristic numbers

$$\alpha_1 - \kappa^2, \alpha_2 - \kappa^2, \ldots, \alpha_s - \kappa^2$$

of the quadratic form

$$K(x, x) - \kappa^2 E(x, x)$$

one and only one is zero, the others negative;

$$0 = \alpha_1 - \kappa^2 > \alpha_2 - \kappa^2 \geqslant \ldots \geqslant \alpha_s - \kappa^2$$

or, combining this result with (3.8.4)

$$\kappa^2 = \alpha_1 > \alpha_2 \geqslant \ldots \geqslant \alpha_s > 0. \tag{3.8.6}$$

b) *Simplification of the Formula for Viscosity.*

We now turn to the practical problem of calculating the expression (3.6.3) for the viscosity:

$$\eta^* = -\frac{1}{15}\mathbf{u}(\mathbf{A}^{1/2} + \kappa)^{-2}\mathbf{t}. \tag{3.8.7}$$

Since matrix relations like $A + B = C$ and $AB = F$ are invariant against transformations of the type

$$A \rightarrow T\,A\,T^{-1}, \text{ e.g.}$$

$$T\,A\,T^{-1}\,T\,B\,T^{-1} = T(AB)T^{-1},$$

we may express our formula (3.8.7) for viscosity as follows:

$$-15\eta^* = \mathbf{u}\,\mathbf{R}^{-1}\,(\mathbf{K}^{1/2} + \kappa)^{-2}\,\mathbf{R}\,\mathbf{t} \tag{3.8.8}$$

$$= \mathbf{u}\,\mathbf{R}^{-1}\,\mathbf{L}'\,(\mathbf{D}^{1/2} + \kappa)^{-2}\,\mathbf{L}\mathbf{R}\,\mathbf{t}. \tag{3.8.9}$$

It is impossible in general to obtain an explicit expression for the transformation L and for the characteristic values $\alpha_1, \ldots, \alpha_s$. However, the knowledge of α_1 and the corresponding eigenvector (3.8.5) will enable us to isolate a term that yields the major contribution to the final result, and to simplify the calculation of the remainder.

This simplification depends on a relation between the rather complicated vector $\mathbf{Rt}$ and a vector $\mathbf{m}$

$$m_j = \frac{e_j}{\omega_j}\sqrt{\frac{n_j}{\omega_j}} \tag{3.8.10}$$

which appeared during a systematic study of the product in (3.8.7). The components of $\mathbf{Rt}$ are, by (3.8.1) and (3.5.2)

$$R_{jj}t_j = -\frac{4\pi}{\kappa(DkT)^2}e_j\sqrt{\frac{n_j}{\omega_j}}\sum_i\frac{n_ie_i^2}{\omega_i + \omega_j}. \tag{3.8.11}$$

---

[1] That is, the vector such that $\mathbf{Kx} = \alpha_1\mathbf{x}$, i.e. operation on $\mathbf{x}$ with $\mathbf{K}$ is equivalent to multiplying $\mathbf{x}$ with the (scalar) characteristic number $\alpha_1 = \kappa^2$. The components l_{1j} of l_1 are the elements of the first row of L.

The scalar product[1] of **Rt** and the eigenvector $\mathbf{l}_1$ is

$$(\mathbf{l}_1\,\mathbf{Rt}) = -\frac{4\pi}{\kappa(DkT)^2}\sum_{ji} e_j\sqrt{\frac{n_j}{\omega_j}}\,e_j\sqrt{\frac{n_j}{\omega_j}}\,\frac{n_i e_i^2}{\omega_i+\omega_j}\Big/\left(\sum_k \frac{n_k e_k^2}{\omega_k}\right)^{1/2}$$

$$= -\frac{4\pi}{\kappa(DkT)^2}\sum_{ji}\frac{n_j e^2{}_j n_i e_i^2}{\omega_j(\omega_i+\omega_j)}\Big/\left(\sum_k \frac{n_k e_k^2}{\omega_k}\right)^{1/2}$$

$$= -\frac{2\pi}{\kappa(DkT)^2}\left(\sum_i \frac{n_i e_i^2}{\omega_i}\right)^{3/2} \qquad (3.8.12)$$

and then the part of **Rt** that is "parallel" $\mathbf{l}_1$ is given by

$$(\mathbf{l}_1\,\mathbf{Rt})l_{1j} = -\frac{2\pi}{\kappa(DkT)^2}e_j\sqrt{\frac{n_j}{\omega_j}}\sum_i\frac{n_i e_i^2}{\omega_i}. \qquad (3.8.13)$$

The remainder of **Rt** with the components

$$R_{jj}t_j - (\mathbf{l}_1\mathbf{Rt})\,l_{1j} = -\frac{4\pi}{\kappa(DkT)^2}e_j\sqrt{\frac{n_j}{\omega_j}}\sum_i n_i e_i^2\left(\frac{1}{\omega_i+\omega_j}-\frac{1}{2\omega_i}\right)$$

$$= \frac{2\pi}{\kappa(DkT)^2}e_j\sqrt{\frac{n_j}{\omega_j}}\sum_i\frac{n_i e_i^2}{\omega_i}\,\frac{\omega_j-\omega_i}{\omega_j+\omega_i} \qquad (3.8.14)$$

is "perpendicular" to $\mathbf{l}_1$, i.e.

$$(\mathbf{l}_1\{\mathbf{Rt} - (\mathbf{l}_1\,\mathbf{Rt})\,\mathbf{l}_1\}) = 0.$$

Let us now evaluate $(\mathbf{K} - \kappa^2)\,\mathbf{m}$:

$$\frac{DkT}{4\pi}(\mathrm{K}-\kappa^2)_{j\sigma}m_\sigma = \sqrt{\frac{n_j}{\omega_j}}\,\frac{e_j}{\omega_j}\sum_i\frac{n_i e_i^2\,\omega_i}{\omega_i+\omega_j} + \sum_i\sqrt{\frac{n_i}{\omega_i}}\,\frac{e_i}{\omega_i}\,\frac{e_j e_i\sqrt{n_j n_i \omega_j \omega_i}}{\omega_i+\omega_j}$$

$$-\sqrt{\frac{n_j}{\omega_j}}\,\frac{e_j}{\omega_j}\sum_i n_i e_i^2$$

$$= e_j\sqrt{\frac{n_j}{\omega_j}}\sum_i\frac{n_i e_i^2}{\omega_i}\,\frac{\omega_j-\omega_i}{\omega_j+\omega_i}. \qquad (3.8.15)$$

By comparing (3.8.14) and (3.8.15), it is immediately apparent that

$$\mathbf{Rt} - (\mathbf{l}_1\mathbf{Rt})\mathbf{l}_1 = \frac{1}{2\kappa DkT}(\mathbf{K}-\kappa^2)\,\mathbf{m}, \text{ or}$$

$$\mathbf{Rt} = \frac{1}{2\kappa DkT}(\mathbf{K}-\kappa^2)\,\mathbf{m} + (\mathbf{l}_1\,\mathbf{Rt})\,\mathbf{l}_1. \qquad (3.8.16)$$

The vector **Rt** is thus expressed in terms of the vector **m** and the eigenvector $\mathbf{l}_1$. This result substituted in (3.8.8) gives

---

[1] We use the conventional notation (a,b) to denote the scalar product $a_\sigma b_\sigma$ of two vectors.

$$-15\eta^* = \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-2}\left(\frac{(\mathbf{K} - \kappa^2)\,\mathbf{m}}{2\kappa\, DkT} + (\mathbf{l}_1\,\mathbf{Rt})\,\mathbf{l}_1\right)$$
$$= \mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-2}(\mathbf{l}_1\mathbf{Rt})\mathbf{l}_1 + \frac{1}{2\kappa\, DkT}\mathbf{uR}^{-1}(\mathbf{K}^{1/2} + \kappa)^{-1}(\mathbf{K}^{1/2} - \kappa)\mathbf{m}. \tag{3.8.17}$$

Since $\mathbf{l}_1$ is the eigenvector corresponding to the characteristic number $\alpha_1 = \kappa^2$, the first term of (3.8.17),

$$(\mathbf{l}_1\,\mathbf{Rt})\mathbf{uR}^{-1}\,\mathbf{L}'\,(\mathbf{D}^{1/2} + \kappa)^{-2}\,\mathbf{L}\,\mathbf{l}_1$$

reduces to $(\mathbf{l}_1\mathbf{Rt})\mathbf{uR}^{-1}\mathbf{L}'\,(\alpha_1^{1/2} + \kappa)^{-2}\,\mathbf{Ll}_1 = \dfrac{(\mathbf{l}_1\mathbf{Rt})}{4\kappa^2}\mathbf{uR}^{-1}\,\mathbf{l}_1$ due to the orthogonality of the transformation L:

$$Ll_1 = l_{j\sigma}l_{1\sigma} = \delta_{j1}.$$

This term may now be readily evaluated by (3.8.12), (3.8.1), (3.8.5) and (3.8.4b).

$$\frac{(\mathbf{l}_1\,\mathbf{Rt})}{4\kappa^2}\mathbf{uR}^{-1}\,\mathbf{l}_1 = \frac{-1}{8\kappa DkT}\sum_i \frac{n_i e_i^2}{\omega_i}. \tag{3.8.18}$$

We shall show in the next paragraphs that the second term in (3.8.17) is the previously mentioned correction term. That is, the term just evaluated is the main contribution to η^*, and in fact, for the simple case where

$$\omega_1 = \omega_2 = \omega_3 \ldots = \omega$$

the correction term vanishes, and

$$\eta^* = \frac{1}{120\kappa\, DkT}\sum_i \frac{n_i e_i^2}{\omega_i} = \frac{\kappa}{480\,\pi\omega} \tag{3.8.19}$$

which is the result announced in the introduction (3.1.3).

c. *Calculation of Correction Term in* (3.8.17).

First of all, we note that the correction term

$$\delta\eta^* = \frac{-1}{30\,\kappa\, DkT}\mathbf{u}\,\mathbf{R}^{-1}\,(\mathbf{K}^{1/2} + \kappa)^{-1}\,(\mathbf{K}^{1/2} - \kappa)\,\mathbf{m}$$
$$= \frac{-1}{30\,\kappa\, DkT}\mathbf{uR}^{-1}\,\mathbf{L}'(\mathbf{D}^{1/2} + \kappa)^{-1}\,(\mathbf{D}^{1/2} - \kappa)\,\mathbf{L}\,\mathbf{m} \tag{3.8.20}$$

vanishes when the largest characteristic number $\alpha_1 = d_{11} = \kappa^2$ is substituted in place of $\mathbf{K}$. Therefore, we may add to $\mathbf{m}$ or $\mathbf{uR}^{-1}$ any multiple of $\mathbf{l}_1$ (since $(\mathbf{D}^{1/2} - \kappa)\,\mathbf{Ll}_1 = 0$ always), which will permit us to express (3.8.20) in a more convenient form for numerical computation. Thus if we define two vectors $\mathbf{p}$ and $\mathbf{q}$ by

$$q_j = m_j - (\mathbf{m}, \mathbf{l}_1)\,l_{1j} = e_j\sqrt{\frac{n_j}{\omega_j}}\left(\frac{1}{\omega_j} - \sum_i \frac{n_i e_i^2}{\omega_i^2}\Big/\sum_i \frac{n_i e_i^2}{\omega_i}\right)$$
$$= e_j\sqrt{n_j/\omega_j}\,(\rho_j - \overline{\rho^2}/\overline{\rho}) \tag{3.8.21}$$

and

$$p_j = u_j\,R^{-1}{}_{jj} - (\mathbf{uR}^{-1}\,\mathbf{l}_1)\,l_{1j} = e_j\sqrt{n_j\omega_j} - e_j\sqrt{n_j/\omega_j}\sum_i n_i e_i^2\Big/\sum_i n_i e_i^2/\omega_i$$
$$= e_j\sqrt{n_j/\omega_j}\,\,(1/\rho_j - 1/\overline{\rho}), \tag{3.8.22}$$

p and **q** may replace **m** and $\mathbf{uR}^{-1}$ in (3.8.20) without changing the latter. The symbols $\bar{\rho}$ and $\overline{\rho^2}$ are obvious abbreviations for the averages of $\rho_j = 1/\omega_j$ and ρ_j^2, averaged with respect to the ionic strength. For the case when all the mobilities are equal, (3.8.21) and (3.8.22) vanish and the correction term becomes zero; this fact is also clear from (3.8.5) and (3.9.10), which show that for this case, **m** becomes proportional to the eigenvector $\mathbf{1}_1$, and then $(\mathbf{D}^{1/2} - \kappa)$ **Lm** vanishes. Introducing the results of the above steps

$$\begin{aligned}\delta\eta^* &= \frac{-1}{30\,\kappa DkT}\,\mathbf{p}(\mathbf{K}^{1/2} + \kappa)^{-1}\,(\mathbf{K}^{1/2} - \kappa)\mathbf{q} \\ &= \frac{-1}{30\,\kappa DkT}\,\mathbf{p}(1 - 2\{1 + \kappa^{-1}\,\mathbf{K}^{1/2}\}^{-1})\mathbf{q}. \qquad (3.8.23)\end{aligned}$$

d) *Power Series Expansion.*

As a starting-point for expanding the matrix **K** in a power series, we note that a function

$$f(D) \equiv \begin{pmatrix} f(\alpha_1) & 0 & . & . & 0 \\ 0 & f(\alpha_2) & . & . & 0 \\ . & . & . & . & . \\ 0 & 0 & . & & f(\alpha_s) \end{pmatrix}$$

of the diagonal matrix

$$D = \begin{pmatrix} \alpha_1 & . & . & . & . & 0 \\ 0 & \alpha_2 & . & . & . & 0 \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & \alpha_s \end{pmatrix} = (\alpha_j \delta_{ji})$$

may be expanded in a Taylor series by expanding the elements

$$f(\alpha_j) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}\,(\alpha_j - a)^n = \sum_{n=0}^{\infty} c_n\,(\alpha_j - a)^n$$

provided that this series converges for $\alpha_j = \alpha_1, \ldots, \alpha_s$. The series may be written in matrix form

$$f(\mathbf{D}) = \sum_{n=0}^{\infty} c_n\,(\mathbf{D} - a\,\mathbf{1})^n.$$

Now if

$$K = L^{-1}DL,$$

(where, if L be orthogonal, $L^{-1} = L'$), and if we adopt the evidently self-consistent definition of a matrix function

$$\mathrm{f}(\mathrm{K}) = L^{-1}f(D)L,$$

whereby e.g.

$$\mathbf{K}^n = \mathbf{L}^{-1}\,\mathbf{D}^n\,\mathbf{L}$$

we shall have

$$f(\mathbf{K}) = \mathbf{L}^{-1}f(\mathbf{D})\mathbf{L} = \sum_{n=0}^{\infty} c_n\,(\mathbf{K} - a\,\mathbf{1})^n,$$

provided that this series converges for every characteristic number of K, substituted in the place of K. We are particularly interested in the function

$$f(\kappa^{-2}\mathbf{K}) = 1 - 2(1 + \kappa^{-1}\,\mathbf{K}^{1/2})^{-1}. \qquad (3.8.24)$$

The Taylor expansion of $f(z)$ around $a = 1/2$ is, with

$$z = \tfrac{1}{2} + t; t = 2z - 1$$

$$\begin{aligned}
(1 + \sqrt{z})^{-1} &= (1 - z)^{-1} - \sqrt{z}\,(1 - z)^{-1} \\
&= 2(1 - 2t)^{-1} - \sqrt{2}\,(1 + 2t)^{1/2}\,(1 - 2t)^{-1} \\
&= \sqrt{2}\,\left\{\sqrt{2}\sum_{n=0}^{\infty}(2t)^n - \sum_{p=0}^{\infty}\binom{1/2}{p}(2t)^p\sum_{q=0}^{\infty}(2t)^q\right\} \\
&= \sqrt{2}\,\left\{\sqrt{2}\sum_{n=0}^{\infty}(2t)^n - \sum_{n=0}^{\infty}(2t)^n\sum_{p=0}^{n}\binom{1/2}{p}\right\} \\
&= \sum_{n=0}^{\infty}\sqrt{2}\left\{\sqrt{2} - \sum_{p=0}^{n}\binom{1/2}{p}\right\}(2z - 1)^n
\end{aligned}$$

or with

$$c_0 = 1 - 2\sqrt{2}\,(\sqrt{2} - 1) = -3 + 2\sqrt{2}$$

$$c_n = -\,2\sqrt{2}\left\{\sqrt{2} - \sum_{p=0}^{n}\binom{1/2}{p}\right\}, n \geqslant 1$$

$$1 - 2\,(1 + \sqrt{z})^{-1} = \sum_{n=0}^{\infty} c_n\,(2z - 1)^n \qquad (3.8.25)$$

$$\begin{array}{llll}
c_0 = & -0.1716 & c_3 = & 0.0659 \\
c_1 = & 0.2427 & c_4 = & -0.0447 \\
c_2 = & -0.1109 & c_5 = & 0.0325
\end{array}$$

convergent in the interval $0 \leqslant z \leqslant 1$.

According to (3.8.6), the characteristic numbers $\alpha_1/\kappa^2, \ldots, \alpha_s/\kappa^2$ of our matrix $\kappa^{-1}\mathbf{K}$ are all in this range. Of course, for the largest, $\alpha_1 = \kappa^2$, the convergence will be slow; however, the vector $\mathbf{q} = \mathbf{m} - \mathbf{l}_1(\mathbf{l}_1\mathbf{m})$, to which the operator series will be applied, is orthogonal to $\mathbf{l}_1$, so that the misbehavior of α_1 in the expansion

$$\sum_{n=0}^{\infty} c_n\,(2\kappa^{-2}\mathbf{K} - \mathbf{1})^n\mathbf{q} = \sum_{n=0}^{\infty} c_n \sum_{p=1}^{s} \mathbf{l}_p\,(2\kappa^{-2}\alpha_p - 1)^n(\mathbf{l}_p, \mathbf{q}) \qquad (3.8.26)$$

is harmless, because the corresponding terms never enter. The remaining characteristic numbers $\alpha_2, \ldots, \alpha_s$ are ordinarily close enough to $\kappa^2/2$ for the series to converge rapidly.

If we introduce the series expansion (3.8.26) into the correction term (3.8.23), we obtain

$$\begin{aligned}
\delta\eta^* &= \frac{-1}{30\kappa DkT}\,\mathbf{p}\sum_{n=0}^{\infty} c_n\,(2\kappa^{-2}\mathbf{K} - \mathbf{1})^n\,\mathbf{q} \\
&= \frac{-1}{30\kappa DkT}\,\mathbf{p}\sum_{n=0}^{\infty} c_n\,\mathbf{q}^{(n)} \qquad (3.8.27)
\end{aligned}$$

where $\mathbf{q}^{(n)}$ is given by the recursion formula

$$\mathbf{q}^{(0)} = \mathbf{q}$$
$$\mathbf{q}^{(n)} = (2\kappa^{-2}\mathbf{K} - \mathbf{1})\,\mathbf{q}^{(n-1)}$$

and

$$p_j = e_j \sqrt{n_j/\omega_j}\,(1/\rho_j - 1/\bar{\rho})$$
$$q_j = e_j \sqrt{n_j/\omega_j}\,(\rho_j - \overline{\rho^2}/\bar{\rho}).$$

The total electrostatic contribution to viscosity is then

$$\eta^* = \frac{1}{120\,\kappa\,DkT}\left(\sum_i \frac{n_i e_i^2}{\omega_i} - 4\,(\mathbf{p}, \{\sum_{n=0}^{\infty} c_n\,\mathbf{q}^{(n)}\})\right). \qquad (3.8.28)$$

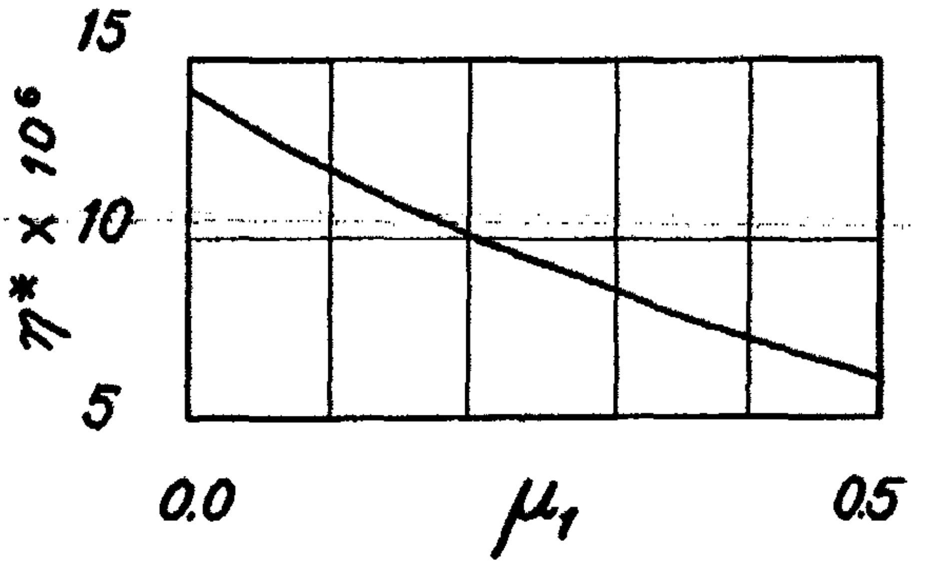

FIG. 3
Electrostatic Contribution to Viscosity of HCl-KCl Mixtures

e) *Calculation for a Simple Electrolyte.*

For $s = 2$, our formula (3.8.17) gives the result obtained by Falkenhagen. The characteristic values of K, obtained by solving the secular equation, are

$$\alpha_1 = \kappa^2, \alpha_2 = q\kappa^2,$$

where

$$q = \frac{n_1 e_1^2\,\omega_1 + n_2 e_2^2\,\omega_2}{(n_1 e_1^2 + n_2 e_2^2)\,(\omega_1 + \omega_2)}. \qquad (3.8.29)$$

Now in evaluating our viscosity formula

$$\eta^* = \frac{1}{120\,\kappa\,DkT}\left(\frac{n_1 e_1^2}{\omega_1} + \frac{n_2 e_2^2}{\omega_2} - 4\,\mathbf{p}\,(1 - \{2\,\kappa^{-1}\mathbf{K} + \mathbf{1}\}^{-1})\,\mathbf{q}\right),$$

we remember that $\mathbf{q}$ is orthogonal to $\mathbf{l}_1$, which means parallel to $\mathbf{l}_2$. Consequently,

$$f(\mathbf{K})\,\mathbf{q} = f(\alpha_2)\,\mathbf{q}$$

and the correction term becomes

$$-\,4\,\mathbf{p}\,f(\alpha_2)\,\mathbf{q} = -\,4 f(\alpha_2)\,(\mathbf{p}, \mathbf{q})$$

Substituting our values

$$f(\alpha_2) = \frac{q - 1}{(\sqrt{q} + 1)^2}$$

$$(\mathbf{p}, \mathbf{q}) = \frac{-n_1 e_1^2\, n_2 e_2^2\, (\omega_1 - \omega_2)^2}{(n_1 e_1^2\, \omega_2 + n_2 e_2^2\, \omega_1)\omega_1 \omega_2}$$

whence

$$-4\, f(\alpha_2)\, (\mathbf{p}, \mathbf{q}) = \frac{-4\, n_1 e_1^2\, n_2 e_2^2\, (\omega_1 - \omega_2)^2}{(n_1 e_1^2 + n_2 e_2^2)\, (\omega_1 + \omega_2)\, (\omega_1 \omega_2)\, (\sqrt{q} + 1)^2}$$

$$= \frac{-4 \quad z_1 z_2 \quad (\rho_2 - \rho_1)^2}{(\sqrt{q} + 1)^2\, (z_1 + z_2)^2\, (\rho_1 + \rho_2)}$$

where z_1 and z_2 are the valences of the ions.
Then

$$\eta^* = \frac{\kappa}{480\pi}\left((1 - q)\,(\rho_1 + \rho_2) - \frac{4}{(\sqrt{q} + 1)^3}\, \frac{z_1 z_2}{(z_1 + z_2)^2}\, \frac{(\rho_2 - \rho_1)^2}{(\rho_1 + \rho_2)}\right) \tag{3.8.30}$$

f) *Conversion to Practical Units.*

Numerical computation of η^* by the formula (3.8.17) is simplified by introducing the ionic strength

$$\Gamma_i = m_i\, z_i^2 = \frac{1000}{N\epsilon^2} n_i\, e_i^2, \tag{3.8.31}$$

where m_i is concentration in mols per liter and z_i is the valence. (N = Avogadro's number, ϵ = electronic charge). We define the relative ionic strength μ_i by

$$\mu_i = \frac{\Gamma_i}{\Gamma} = \frac{n_i\, e_i^2}{\sum\limits_i n_i\, e_i^2} \tag{3.8.32}$$

so that

$$\kappa^2 = \frac{N^2 \epsilon^2}{1000}\, \frac{4\pi}{DRT}\, \Gamma. \tag{3.8.33}$$

Then by the transformation

$$\begin{gathered} \mathrm{M\, K\, M^{-1} = G'} \\ m_{ji} = \delta_{ji} e_j \sqrt{n_j \omega_j} \end{gathered} \tag{3.8.34}$$

we obtain a new matrix[1] G' with elements

$$g'_{ji} = \frac{4\pi}{DkT}\left(\delta_{ji} \sum_i n_i e_i^2\, \frac{\omega_i}{\omega_i + \omega_j} + n_j e_j^2\, \frac{\omega_j}{\omega_i + \omega_j}\right).$$

Then since $\kappa^{-2}\,\mathbf{K}$ appears in (3.8.26), we introduce a new matrix H' whose elements are pure numbers

---

[1] We write $G' = (g'_{ji}) = (g_{ij})$ for this matrix, because the transposed matrix $G = (g_{ji})$ appears in the conductance problem, and will be used more frequently.

$$h'_{ji} = \frac{g'_{ji}}{\kappa^2} = \left(\delta_{ji}\sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_j \frac{\omega_j}{\omega_i + \omega_j}\right). \qquad (3.8.35)$$

Now ρ_j was defined as the friction coefficient for an ion of the j-th species, so that

$$\frac{1}{\rho_j} = \omega_j = \frac{u_j}{|e_j|}. \qquad (3.8.36)$$

where u_j is the mobility per unit field in electrostatic units. The mobility $\bar{u}_j$ for a field of one volt per centimeter is accordingly $u_j/300$ and

$$\omega_j = \frac{300\,\bar{u}_j}{\epsilon\ z_j} \qquad (3.8.37)$$

If Λ_j is the equivalent conductance,

$$\Lambda_j = 96\,500\,\bar{u}_j \qquad (3.8.39)$$

and

$$\omega_j = \frac{300}{96\,500}\frac{\Lambda_j}{z_j}, \qquad (3.8.40)$$

also

$$\frac{\omega_i}{\omega_i + \omega_j} = \frac{\Lambda_i/z_i}{\Lambda_i/z_i + \Lambda_j/z_j}, \text{ a pure number.} \qquad (3.8.41)$$

Then

$$h'_{ji} = \delta_{ji}\sum_i \mu_i \frac{\Lambda_i/z_i}{\Lambda_i/z_i + \Lambda_j/z_j} + \mu_j \frac{\Lambda_j/z_j}{\Lambda_i/z_i + \Lambda_j/z_j}.$$

If we now apply the transformation (3.8.34) to (3.8.27), and substitute (3.8.35), we obtain

$$\mathbf{p}\sum_{n=0}^{\infty} c_n\,(2\kappa^{-2}\mathbf{K} - \mathbf{1})^n\,\mathbf{q} = \mathbf{p}\,\mathbf{M}^{-1}\sum_{n=0}^{\infty} c_n\,(2\mathbf{H}' - 1)\,\mathbf{Mq},$$

where

$$(\mathbf{pM}^{-1})_j = \frac{\bar{\rho} - \rho_j}{\rho}$$

and

$$(\mathbf{Mq})_j = n_j e_j^2\,(\rho_j - \overline{\rho^2}/\rho) = \frac{DkT\kappa^2}{4\pi}\mu_j(\rho_j - \overline{\rho^2}/\bar{\rho}).$$

This may be simplified by defining two new vectors

$$r_j = 1 - \rho_j/\bar{\rho} = 1 - \frac{z_j/\Lambda_j}{\overline{z/\Lambda}} \qquad (3.8.42)$$

$$s_j = \mu_j\left(z_j/\Lambda_j - \overline{(z/\Lambda)^2}\Big/\overline{(z/\Lambda)}\right), \qquad (3.8.43)$$

for then

$$\delta\eta'' = \frac{-\kappa}{120\pi}\,\frac{96\,500}{300}\,\epsilon\,\mathbf{r}\sum_{n=0}^{\infty} c_n\,\mathbf{s}^{(n)} \qquad (3.8.44)$$

where $\mathbf{s}^{(n)}$ is defined by the recursion formula

$$s^{(0)} = \mathbf{s}; \mathbf{s}^{(n)} = (2\mathbf{H}' - 1)\,\mathbf{s}^{(n-1)}. \tag{3.8.45}$$

Combining the values for the two terms of η^*,

$$\eta^* = \frac{\kappa}{480\pi}\;\frac{96\;500\,\epsilon}{300}\left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4\mathbf{r}\sum_{n=0}^{\infty} c_n\,\mathbf{s}^{(n)}\right), \tag{3.8.46}$$

which on substituting (3.8.33) for κ becomes

$$\eta^* = \frac{965\;N\epsilon^2}{144\sqrt{250\pi}}\sqrt{\frac{\Gamma}{DRT}}\left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4\mathbf{r}\sum_{n=0}^{\infty} c_n\,\mathbf{s}^{(n)}\right)$$

$$= 0.362\left(\frac{\Gamma}{DT}\right)^{1/2}\left(\sum_i \frac{\mu_i z_i}{\Lambda_i} - 4\mathbf{r}\sum_{n=0}^{\infty} c_n\,\mathbf{s}^{(n)}\right). \tag{3.8.47}$$

3.9. *Appendix II.* Mechanism of Force Transfer.

a) *Statement of Problem.*

In our preliminary discussion (§3.1), we showed that a velocity gradient in a flowing electrolyte produced a stationary deformation of the ionic atmospheres on account of the finite time of relaxation of the latter, and that an additional force transfer between volume elements appeared, due to the resulting asymmetry of the potentials of the ionic atmospheres. We then demonstrated that this additional force corresponds to an increase in the force per unit volume:

$$\mathbf{F}^* = \eta^*\,\Delta\mathbf{v}. \tag{3.9.1}$$

Now if our assumptions have been consistent, this force should be derivable from the potentials ψ_j: the x component of the force acting on a j-ion due to the asymmetry of its atmosphere is

$$-\,e_j\left(\frac{\partial\psi'_j}{\partial x}\right)_{r=0}$$

and therefore the net force per unit volume containing n_j ions of species $1, \ldots, s$ is

$$\mathbf{F}^*_x = -\sum_j n_j e_j\left(\frac{\partial\psi'_j}{\partial x}\right)_{r=0}. \tag{3.9.2}$$

We shall calculate the potentials ψ'_j for the simple case where

$$s = 2;\; n_1 = n_2 = n;\; e_1 = -e_2 = e;\; \omega_1 = \omega_2 = \omega \tag{3.9.3}$$

and carry out the operations indicated in (3.9.2). The result will be identical with that obtained from (3.9.1) by substituting (3.2.2) for the velocity:

$$\mathbf{F}^*_x = b^1_{\mu\mu}\eta^* \tag{3.9.4}$$

and we shall have gained exact information concerning the transfer of stress by the interionic forces.

We recall that the potential ψ'_j was given by

$$\psi'_j\,(\mathbf{r}_1, \mathbf{r}_{12}) = b^{\lambda}{}_{\mu\mu}\, D_{\lambda}\, v_j\,(r) + c^{\mu}{}_{\nu}\, D^2{}_{\mu\nu}\xi_j\,(r) + \tfrac{1}{2}b^{\lambda}{}_{\mu\nu}D^3{}_{\lambda\mu\nu}\,\mu_j(r). \qquad (3.9.5)$$

The even part of the potential $\xi_j(r)$ has already been determined for the general case (3.5.13); we shall first compute its value for our special case (3.9.3), and then the functions $u_j\,(r)$ and $v_j(r)$ must be obtained by solving (3.4.4) and (3.4.6).

b) *Distribution Functions and Potentials.*

According to (3.5.13) and (3.8.3)

$$\xi_j(r) = \{\chi(r, B)\}_{j\sigma}\, t_{\sigma} = T^{-1}{}_{j\mu}\,\{\chi(r, D)\}_{\mu}\, T_{\mu\sigma}\, t_{\sigma} \qquad (3.9.6)$$

where the matrix D (cf. 3.8.29) is

$$\mathrm{D} = \begin{pmatrix} \kappa^2 & 0 \\ 0 & \kappa^2/2 \end{pmatrix}.$$

In order to obtain $T = LR$, we take from (3.8.5) the components of the eigenvector $\mathbf{l}_1$

$$l_{1j} = e_j/\sqrt{2e^2};\ l_{11} = 1/\sqrt{2},\ l_{12} = -1/\sqrt{2}$$

and from the symmetry and orthogonality conditions (3.8.3b),

$$l_{22} = -l_{11} = -1/\sqrt{2} \text{ and } l_{21} = l_{12} = -1/\sqrt{2}$$

so that

$$L = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ -1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}.$$

Then since $T = LR$, i.e. $t_{ij} = l_{i\sigma}r_{\sigma j} = \sqrt{n/\omega}\,l_{ij}$ and $TT^{-1} = 1$,

$$T = \begin{pmatrix} \sqrt{\dfrac{n}{2\omega}} & -\sqrt{\dfrac{n}{2\omega}} \\ -\sqrt{\dfrac{n}{2\omega}} & -\sqrt{\dfrac{n}{2\omega}} \end{pmatrix}, \quad T^{-1} = \begin{pmatrix} \sqrt{\dfrac{\omega}{2n}} & -\sqrt{\dfrac{\omega}{2n}} \\ -\sqrt{\dfrac{\omega}{2n}} & -\sqrt{\dfrac{\omega}{2n}} \end{pmatrix}.$$

The components of $\mathbf{t}$ are

$$t_1 = \frac{-\kappa e}{2\omega DkT} = -t_2.$$

On substituting these values in (3.9.6), we obtain

$$\xi_j(r) = \frac{-\kappa e_j}{2\omega\, DkT}\chi(r, \kappa^2).$$

The expression $\chi(r, \beta^2)$ given in (3.5.10) becomes indeterminate for $\beta^2 = \kappa^2$, but may be immediately evaluated by noting that

$$\lim_{\beta\to\kappa}\frac{\partial}{\partial\kappa}\left(\frac{f(\beta) - f(\kappa)}{\beta - \kappa}\right) = \tfrac{1}{2}\,\frac{\partial^2 f(\kappa)}{\partial\kappa^2}$$

whence

$$\xi_j\,(r) = \frac{-e_j\kappa}{4\omega DkT}\frac{\partial}{\partial\kappa}\left(\frac{e^{-\kappa r} - 1}{\kappa^4 r} + \frac{e^{-\kappa r}}{2\,\kappa^3}\right) = \frac{-e_j\kappa}{2\,\omega DkT}X(r). \qquad (3.9.7)$$

The term in $\left(\frac{\partial \psi'_j}{\partial q^m}\right)$ corresponding to $\xi_j(r)$ is found to be

$$(c^\mu{}_m q^\mu + c^m{}_\nu q^\nu)\frac{\mathrm{d}^2\,\xi_j}{(r\,\mathrm{d}r)^2} + c^\mu{}_\nu q^\mu q^\nu q^m\,\frac{\mathrm{d}^3\xi_j(r)}{(r\,\mathrm{d}r)^3} \tag{3.9.8}$$

by carrying out the differentiation indicated by $D^3{}_{\mu\nu m}$ and noting the relations (3.2.4). This contribution to the directed force should vanish because it is due to the part of the potential that is even in the coordinates, and indeed, since

$$\frac{\mathrm{d}^2\,X(r)}{(r\,\mathrm{d}r)^2} = \tfrac{1}{4}\sum_{n=0}^{\infty}\frac{(-\kappa)^n\,r^n}{n!\,(n+5)}$$

and

$$\frac{\mathrm{d}^3\,X(r)}{(r\,\mathrm{d}r)^3} = \tfrac{1}{4}\sum_{n=0}^{\infty}\frac{(-\kappa)^{n+1}\,r^{n-1}}{n!\,(n+6)}$$

we see that this is actually the case in the limit $r = 0$ (and of course $q = 0$) in (3.9.8): the first term is of the order $q\sim r$ and the second of the order r^2.

By means of the corresponding term in the Poisson equation, F_{ji} is eliminated from (3.4.6), giving

$$b^\lambda{}_{\mu\nu}\,D^3{}_{\lambda\mu\nu}\Bigg(\Delta\Delta u_j - \frac{4\pi}{DkT}\sum_i\frac{n_ie_i^2\,\omega_i}{\omega_i+\omega_j}\Delta u_j + \frac{4\pi}{DkT}\sum_i\frac{n_ie_ie_j\omega_j}{\omega_i+\omega_j}\Delta u_i$$
$$- \frac{8\pi}{DkT}\sum_i\frac{n_ie_ie_j\omega_j}{\omega_i+\omega_j}\frac{\mathrm{d}(r\xi_i(r))}{\mathrm{d}r} + \frac{16\pi}{D}\sum_i\frac{e_i\,\omega_j}{n_j\,(\omega_i+\omega_j)}\varphi_{ji}$$
$$+ \frac{4\pi}{DkT}\sum_i\frac{e_i\,\theta(r)}{n_j\,(\omega_i+\omega_j)}\Bigg) = 0.$$

The condition $\omega_1 = \ldots = \omega_s = \omega$ permits φ_{ji} to be eliminated by means of the even term in the Poisson equation, so that

$$b^\lambda{}_{\mu\nu}\,D^3{}_{\lambda\mu\nu}\Bigg(\Delta\Delta u_j - \frac{2\pi}{DkT}\sum_i n_ie_i^2\,\Delta u_j + \frac{2\pi}{DkT}\sum_i n_ie_ie_j\,\Delta u_i$$
$$- \frac{4\pi}{DkT}\sum_i n_ie_ie_j\,\frac{\mathrm{d}(r\,\xi_i(r))}{\mathrm{d}r} - 2\Delta\xi_j + \frac{2\pi}{\omega DkT}\sum_i\frac{e_i\theta(r)}{n_j}\Bigg) = 0. \tag{3.9.9}$$

By differentiating (3.9.7)

$$\Delta\xi_j = \frac{-\kappa e_i}{4\omega\,DkT}\frac{\partial}{\partial\kappa}\left(\frac{e^{-\kappa r}}{2\kappa}\right). \tag{3.9.10}$$

Also

$$\frac{\mathrm{d}\,r\,\xi_i(r)}{\mathrm{d}r} = \frac{\kappa\,e_i}{4\omega\,DkT}\frac{\partial}{\partial\kappa}\left((1+\kappa r)\,\frac{e^{-\kappa r}}{2\kappa^3}\right) \tag{3.9.11}$$

and by the definition in (3.2.6)

$$\theta\,(r) = -\frac{n_i\,n_j\,e_i\,e_j}{\kappa^2\,DkT}\left(r\,e^{-\kappa r} + \frac{e^{-\kappa r}}{\kappa}\right) \tag{3.9.12}$$

(where in view of the boundary conditions discussed in §3.5, several terms have been dropped: compare with (3.4.7) and (3.4.11)). We substitute the "known" functions of r just obtained in (3.9.9), integrate, and perform the summations:

$$\Delta\Delta u_j - \frac{4\pi}{DkT} n\, e^2 \Delta u_j + \frac{2\pi}{DkT} n\, e\, e_j\, (\Delta u_1 - \Delta u_2) =$$
$$= \frac{3e_j}{8\,\omega\, DkT\,\kappa}\left(1 + r\kappa - \frac{r^2\,\kappa^2}{3}\right) e^{-\kappa r}.$$

By giving j the values 1 and 2 and adding the resulting equations, we obtain

$$\Delta(\Delta - \kappa^2/2)\,(u_1 + u_2) = 0$$

whence, by integration and consideration of boundary conditions, $\Delta u_1 = -\Delta u_2$. We thus obtain as the equation determining $u_j\,(r)$

$$\Delta\Delta u_j = \frac{3e_j}{8\,\omega\, DkT\,\kappa}\left(1 + r\kappa - \frac{r^2\,\kappa^2}{3}\right) e^{-\kappa r}$$

which has the solution

$$u_j\,(r) = \frac{3e_j}{8\,\omega\, DkT\,\kappa}\left[\frac{1}{\kappa^5\, r}\left\{16 - e^{-\kappa r}\left(16 + 11\kappa r + 3\kappa^2 r^2 + \frac{\kappa^3\, r^3}{3}\right)\right\}\right]$$
$$= \frac{3\, e_j}{8\,\omega\, DkT\,\kappa}\, Y(r)$$

satisfying the restrictions imposed on the potential for $r = \infty$ and $r = 0$.

The term containing $u_j\,(r)$ in the formula (3.9.2) for the force equals

$$\tfrac{1}{2}\, b^{\lambda}{}_{\mu\nu}\, D^4{}_{\lambda\mu\nu m}\, u_j\,(r) = \tfrac{1}{2}\, b^{m}{}_{\mu\mu} \frac{\mathrm{d}^2\, u_j\,(r)}{(r\, \mathrm{d}r)^2} + O(r^2)\frac{\mathrm{d}^3\, u_j\,(r)}{(r\,\mathrm{d}r)^3}$$
$$+ O(r^4)\frac{\mathrm{d}^4\, u_j\,(r)}{(r\,\mathrm{d}r)^4}$$

where the notation $O(r^2)$ means a coefficient of the order of r^2. If, as before, we write $Y(r)$ as a series and differentiate, we find

$$\frac{\mathrm{d}^2 Y(r)}{(r\,\mathrm{d}r)^2} = -\sum_{n=0}^{\infty}\frac{(-\kappa)^n\, r^n\,(n-1)}{n!\,3\,(n+5)}$$
$$\frac{\mathrm{d}^3 Y(r)}{(r\,\mathrm{d}r)^3} = -\sum_{n=0}^{\infty}\frac{(-\kappa)^{n+2}\, r^n}{n!\,3\,(n+7)} = O(1)_{r=0}$$

and

$$\frac{\mathrm{d}^4 Y(r)}{(r\,\mathrm{d}r)^4} = \sum_{n=0}^{\infty}\frac{(-\kappa)^{n+3}\, r^{n-1}}{n!\,3\,(n+8)} = O(r^{-1})_{r=0}$$

so that in the limit $r = 0$, we have

$$\left(\tfrac{1}{2}\, b^{\lambda}{}_{\mu\mu}\, D^4{}_{\lambda\mu\nu m}\, u_j\,(r)\right)_{r=0} = b^{m}{}_{\mu\mu}\,\frac{e_j}{80\,\omega\, DkT\,\kappa}. \qquad (3.9.13)$$

The equations determining $v_j(r)$ are obtained by eliminating G_{ji} from (3.4.4) by means of the corresponding terms from the Poisson equation, which yields

$$b^{\lambda}{}_{\mu\mu} D_{\lambda} \left(\Delta\Delta v_j - \frac{4\pi}{DkT} \sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta v_j + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta v_i \right.$$
$$\left. + \frac{4\pi}{DkT} \sum_i \frac{n_i e_i e_j \omega_j}{\omega_i + \omega_j} \Delta \xi_i - \frac{2\pi}{DkT} \sum_i \frac{e_i \zeta(r)}{n_j (\omega_i + \omega_j)} \right) = 0$$

By a procedure analogous to that used in simplifying the equation for $u_j(r)$, we obtain

$$\Delta\Delta v_j - \frac{4\pi}{DkT} n e^2 \Delta v_j + \frac{2\pi}{DkT} n e e_j (\Delta v_1 - \Delta v_2) =$$

$$= \frac{e_j \kappa}{16 \omega DkT} (3 - \kappa r) e^{-\kappa r}$$

and as before, $\Delta v_1 = -\Delta v_2$. Then

$$\Delta\Delta v_j = \frac{e_j \kappa}{16 \omega DkT} (3 - \kappa r) e^{-\kappa r}. \tag{3.9.14}$$

The solution of (3.9.14) which satisfies the boundary conditions is

$$v_j(r) = \frac{-e_j}{16 \omega DkT} \left(\frac{r e^{-\kappa r}}{\kappa^2} + \frac{5 e^{-\kappa r}}{\kappa^3} + 8 \frac{e^{-\kappa r} - 1}{\kappa^4 r} \right)$$

$$= \frac{-e_j}{16 \omega DkT} Z(r).$$

The term in $\dfrac{\partial \psi'}{\partial q^m}$ corresponding to $v_j(r)$ is

$$b^{\lambda}{}_{\mu\mu} D^2{}_{\lambda m} v_j(r) = b^m{}_{\mu\mu} \frac{d v_j}{r\, dr} + b^{\lambda}{}_{\mu\mu} q^m q^{\lambda} \frac{d^2 v_j}{(r\, dr)^2}.$$

By expanding $Z(r)$ in a power series and differentiating,

$$\frac{d\, Z(r)}{r\, dr} = \sum_{n=0}^{\infty} \frac{(-\kappa)^{n-1} r^n (n-1)(n+1)(n+2)}{(n+3)!}$$

and

$$\frac{d^2 Z(r)}{(r\, dr)^2} = \sum_{n=0}^{\infty} \frac{(-\kappa)^{n+1} r^n}{n!\,(n+5)}.$$

Then in the limit,

$$\left(b^{\lambda}{}_{\mu\mu} D^2{}_{\lambda m} v_j(r)\right)_{r=0} = -b^m{}_{\mu\mu} \frac{e_j}{48 \omega DkT \kappa}. \tag{3.9.15}$$

c) *Calculation of Total Force.*

Combining the results (3.9.13) and (3.9.15),

$$\left(\frac{\partial \psi_j'}{\partial q^m} \right)_{r=0} = -b^m{}_{\mu\mu} \frac{e_j}{120 \omega DkT \kappa}.$$

This result may now be substituted in (3.9.2), whence we obtain

$$F^*_x = -\sum_j n_j e_j \left(\frac{\partial \psi'_j}{\partial x}\right)_{r=0} = b^1{}_{\mu\mu} \frac{\kappa}{480\,\pi\,\omega} = b^1{}_{\mu\mu}\,\eta^*,$$

which is (3.9.4) with the previous value (3.7.3) for the electrostatic viscosity

$$\eta^* = \kappa/480\,\pi\,\omega.$$

4. Conductance and Diffusion

4.1. *Introduction.*

We shall investigate the problem of ions migrating in a general homogeneous field of forces, that is, external forces $\mathbf{k}_1, \ldots, \mathbf{k}_s$ (per ion) acting on ions of the species $1, \ldots, s$, respectively, and a balancing force

$$n_0\,\mathbf{k}_0 = -\sum_{i=1}^{s} n_i\,\mathbf{k}_i \tag{4.1.1}$$

acting on the molecules of the solvent.

We shall show that this system of forces is equivalent to an arbitrary combination of a homogeneous electric field $\mathbf{E} = -\operatorname{grad}\varphi$ and uniform concentration gradients grad $n_1, \ldots$ grad n_s, subject to the restriction of electric neutrality

$$\sum_{i=1}^{s} e_i \operatorname{grad} n_i \equiv \operatorname{grad} \sum_i n_i\,e_i = \operatorname{grad} 0 = 0. \tag{4.1.2}$$

According to thermodynamics, equilibrium could be maintained with this system of field and gradients by introducing further *forces*

$$-\mathbf{k}_0,\ -\mathbf{k}_1, \ldots,\ -\mathbf{k}_s$$

of some other nature, whereby

$$\mathbf{k}_i = -\operatorname{grad}\mu_i = -\operatorname{grad}(\mu'_i + e_i\,\varphi). \tag{4.1.3}$$

Here μ'_i stands for the ordinary thermodynamic potential, and μ_i for the *total potential* of an ion or molecule (without the hypothetical forces $-\mathbf{k}_i$). Now it is safe to assume that the velocities due to different causes of migration may be superimposed; therefore, the velocities caused by the potential gradients $-\operatorname{grad}\mu_i$, $(i = 0, 1, \ldots, s)$ must be the same as those caused by equal forces $\mathbf{k}_0, \mathbf{k}_1, \ldots, \mathbf{k}_s$ (4.1.3), because either will balance the system of forces $-\mathbf{k}_0, -\mathbf{k}_1, \ldots, -\mathbf{k}_s$. On the basis of the Gibbs-Duhem theorem

$$S\,\delta T - V\,\delta p + \sum_i n_i\,\delta\mu'_i = 0$$

(where S = entropy; V = volume; p = pressure), the forces given by (4.1.3) conform to the equilibrium condition (4.1.1), assuming constant temperature and pressure. It is also seen that the free choice of $(s-1)$ concentration

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[1] A system of forces not balancing each other as indicated by (4.1.1) would have to be balanced by a pressure gradient in the liquid. On thermodynamic grounds, the resulting motion of the substances present would be the same if a force equivalent to the pressure gradient were distributed among the molecules and ions in proportion to their partial volumes.

gradients, (grad n_s and grad n_0 being given by (4.1.2) and by the condition grad $p = 0$), and of an electric potential gradient is equivalent to the free choice of s forces $\mathbf{k}_1, \ldots, \mathbf{k}_s$ ($\mathbf{k}_0$ being given by (4.1.1)). The separation of μ_i into two parts μ'_i and $e_i\varphi$ is possible according to molecular theory; but only the sum $\mu_i = \mu'_i + e_i\varphi$ enters into thermodynamic relations, and can be measured by corresponding experiments. For the purposes of thermodynamics, an arbitrary convention about the separation is of course admissible if self-consistent. We have shown above that potential gradients $-$grad μ_i will cause the same migration of ions as equal forces. The "forces" thus defined are evidently not affected by an admissible convention about the electrical contribution to the total potentials, and, conversely, we cannot expect to obtain information about the actual electrostatic potentials from diffusion experiments.

We shall now investigate the effect of interionic forces on the migration of ions. An isolated ion would move relatively to the surrounding solvent with the velocity

$$\mathbf{v}_i = \mathbf{k}_i/\rho_i = \mathbf{k}_i\,\omega_i \tag{4.1.4}$$

where ρ_i is its coefficient of friction, and this law will be approached for very dilute solutions. If we were dealing with molecules instead of ions, and the different kinds of molecules were nearly enough alike to form an ideal solution, then we might expect a law similar to (4.1.4) to hold for finite concentrations as well. In the case of an electrolyte, however, the Coulomb forces between the ions will cause deviations from random distribution in the form of ionic atmospheres, and for this reason, the ions will affect each other's motion.

There are two different effects to be considered, namely the direct transfer of electric forces between the ions and a hydrodynamic effect, the so-called electrophoresis. The latter effect was recognized by Debye and Hückel, while the former had been expected for a long time by those familiar with the properties of electrolytes.

We can get an idea about the force effect and estimate its order of magnitude if we consider one particular ion moving under the action of a force $\mathbf{k}$. Its velocity will be (nearly)

$$\mathbf{v} = \mathbf{k}/\rho.$$

When the ion starts moving, at first its atmosphere will be left behind; but the displaced ion will soon exert an electric pull on its lagging atmosphere, which will continue to form around the ion as it moves along and to scatter in the rear. The ion will maintain a lead of the order τ seconds, where τ is the relaxation time (1.3.4) of the atmosphere, corresponding to a distance

$$\mathbf{v}\tau = \mathbf{k}\tau/\rho.$$

The ratio of this distance to the radius $1/\kappa$ of the ionic atmosphere gives the relative dissymmetry of the latter,

$$\kappa\,\mathbf{k}\,\tau/\rho;$$

thus the directed component $\Delta\mathbf{k}$ of the total force $e^2\kappa/D$ between ion and atmosphere will be of the order

$$-(e^2\kappa^2/D)\kappa\mathbf{k}\tau/\rho = -\mathbf{k}\tau e^2\kappa^3/\rho D$$

retarding the ion. Substituting (1.3.4) for the time of relaxation, we obtain

$$\Delta\mathbf{k} \approx -e^2\kappa\mathbf{k}/DkT = -\kappa d_0\mathbf{k} \tag{4.1.5}$$

(cf. 1.3.3), which indeed agrees with the results to be derived in the following, except for a numerical factor.

By the principle of action and reaction, the force (4.1.5) is taken up by the ions in the atmosphere and, conversely, if some of the ions in the atmosphere are caused to migrate under the influence of external forces, "blowing" part of the structure to one side, the central ion will receive a force on account of the resulting asymmetry. We might also consider the central ion, as forming part of the other ions' atmospheres; the relation of neighborhood is a reciprocal one. In order to make this reciprocity complete, it is necessary to consider the Brownian motion of the central ion, which thereby contributes to the relaxation of its own atmosphere; in our fundamental equations (2.5.7), due allowance has been given for this effect.

The *electrophoresis* is most simply described and estimated for the case of electrical conduction where, for an electric field **E**,

$$\mathbf{k}_0 = 0;\ \mathbf{k}_i = e_i\mathbf{E}.\ (i = 1, \ldots s)$$

The atmosphere of an ion of charge e_j will contain the total electric charge $-e_j$ and consequently be subject to a total force $-\mathbf{E}e_j$ in the field **E**. This force will be taken up by the liquid in which the ions of the atmosphere are embedded, and cause hydrodynamic motion in the direction of the force $-\mathbf{E}e_j$. For an estimate of the effect, we may assume the entire charge $-e_j$ of the atmosphere situated at a distance equal to the mean radius $1/\kappa$, uniformly distributed on a spherical shell. Then according to Stokes' law, the interior of the sphere will move with the velocity

$$\Delta\mathbf{v}_j = -\mathbf{E}e_j/6\pi\eta\kappa^{-1} = -\mathbf{E}e_j\kappa/6\pi\eta \tag{4.1.6}$$

where η = viscosity. The liquid that immediately surrounds the central ion will be moving with the velocity $\Delta\mathbf{v}_j$, and this ion, as it migrates in the electric field, must swim in a countercurrent of the magnitude (4.1.6). If the ion had no atmosphere, it would move with the velocity

$$\mathbf{k}_j/\rho_j = \mathbf{E}e_j/\rho_j.$$

Surrounded by an atmosphere, the ion is subject to a force $\mathbf{k}_j - \Delta\mathbf{k}_j$ (on account of the correction (4.1.5)); but the velocity corresponding to this force, namely

$$(\mathbf{k}_j - \Delta\mathbf{k}_j)/\rho_j$$

describes the motion relative to a neighborhood moving with the velocity $\Delta\mathbf{v}_j$, so that the net velocity will be

$$\mathbf{v}_j = \Delta\mathbf{v}_j + (\mathbf{k}_j - \Delta\mathbf{k}_j)/\rho_j \tag{4.1.7}$$

or in the particular case of electric conduction

$$\mathbf{v}_j = \frac{\mathbf{E}e_j - \Delta\mathbf{k}}{\rho_j} - \frac{\mathbf{E}e_j\kappa}{6\pi\eta}.$$

Incidentally, the formula (4.1.6) gives an exact value for the electrophoretic effect, except for possible refinements, (not affecting the limiting $\sqrt{c}$ formula), applied to the assumed value for the radius of the ionic atmosphere. In the general case of arbitrary forces $\mathbf{k}_0, \mathbf{k}_1, \ldots, \mathbf{k}_s$ there will also be an electrophoretic effect, because the concentrations in the ionic atmosphere differ from the average concentrations $n_1, \ldots, n_s$ in the bulk of the solution, so that the force balance (4.1.1) is upset, and the resulting force density in the atmosphere will cause hydrodynamic motion.

According to (4.1.5) and (4.1.6), both the force effect and the electrophoresis are proportional to the square root of the concentration, on account of the factor $\kappa \sim \sqrt{c}$. The two effects are ordinarily of the same order of magnitude; they change the velocity of an ion of radius b by amounts of the order

$$\kappa d_0 \mathbf{k}/\rho = \mathbf{k}\kappa d_0/6\pi\eta b$$

and

$$\mathbf{k}\kappa/6\pi\eta$$

respectively, and we have already pointed out that according to (1.3.3), $d_0 = e^2/DkT$ is comparable to the radius b of an ordinary ion. For KCl in water at 25°C. and 0.001n concentration, the force effect is 0.75%, the electrophoresis 1.26% of the limiting equivalent conductance.

4.2. *Electrophoresis.*

In this section, we shall review briefly a previous calculation[1] of the decrease in velocity of an ion due to electrophoresis, and extend the treatment to deal with the general problem of ionic migration. In the case of electrolytic conduction, a given ion does not move with respect to a medium at rest, but, since it is surrounded by an atmosphere of ions which move in the opposite direction, it actually travels with respect to a moving medium. If the applied force on a j-ion is $\mathbf{k}_j$, then, as pointed out in the previous paragraph, instead of using the velocity

$$\mathbf{v}_j = \mathbf{k}_j\omega_j$$

to compute transfer of ions (and charge), we must use $\mathbf{v}_j - \Delta\mathbf{v}_j$, where $\Delta\mathbf{v}_j$ is the so-called electrophoretic correction.

The electrophoretic effect is due to a volume force attacking in the liquid that surrounds an ion. If the average concentration of j-ions is n_j, the average applied force on the ions contained in a unit volume of solution is

$$\sum_{j=1}^{s} n_j\mathbf{k}_j = n_\sigma \mathbf{k}_\sigma$$

This force is transferred to the n_0 solvent molecules per unit volume of solution; the equilibrium condition (4.1.1) may be written symmetrically

$$n_\sigma\mathbf{k}_\sigma + n_0\mathbf{k}_0 = 0. \qquad (4.2.1)$$

But the force acting on the ions in an element of volume dV near a j-ion is $n_{j\sigma}\mathbf{k}_\sigma dV$ because the presence of a j-ion changes the average concentrations in

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[1] L. Onsager: Physik. Z., 27, 388 (1926).

dV by electrostatic interaction; the force on the solvent remains $n_o\mathbf{k}_o dV$. Therefore there acts on dV a net force equal to

$$(n_{j\sigma}\mathbf{k}_\sigma + n_o\,\mathbf{k}_o)\,dV = (n_{j\sigma} - n_\sigma)\mathbf{k}_\sigma\,dV. \tag{4.2.2}$$

In calculating the electrophoresis, we shall neglect the asymmetry of the ionic atmospheres.[1]

In spherical coordinates (with the j-ion at the origin), $dV = r^2\,dr\,d\Omega$ so that the force acting on a spherical shell of solution at a distance r from the central ion is

$$4\pi r^2(n_{j\sigma} - n_\sigma)\mathbf{k}_\sigma\,dr\,. \tag{4.2.3}$$

This force is uniformly distributed over the shell and is in the direction of the applied force $\mathbf{k}$. This distribution of forces is the same as that acting on a solid sphere of radius r moving through a liquid of viscosity η. We therefore may apply Stokes' formula

$$\mathbf{V} = \mathbf{P}/6\pi\eta r. \tag{4.2.4}$$

A force $\mathbf{P}$, applied as described, will cause all the points in the interior of the spherical shell to move with the *same* velocity $\mathbf{V}$.

In order to calculate the force density, we must first obtain $(n_{ji} - n_i)$ as a function of r. According to the Boltzmann distribution (and our definition of n_{ji} and ψ_i,

$$n_{ji} = n_i \exp\,(-\,e_i\psi^\circ_j/kT). \tag{4.2.5}$$

In approximating the exponential by its series expansion, we shall retain the term involving e_i^2, because the contribution of the e_i term to diffusion flow will depend on (the square of) the difference of the mobilities of the ions present. To this approximation

$$n_{ji} \approx n_i\left\{1 - \frac{e_i\,\psi^\circ_j}{kT} + \frac{1}{2}\left(\frac{e_i\,\psi^\circ_j}{kT}\right)^2\right\}. \tag{4.2.6}$$

For the potentials, we shall use Debye's second approximation[2]

$$\psi^\circ_j = \frac{e_j}{D}\,\frac{e^{\kappa a}}{1 + \kappa a}\,\frac{e^{-\kappa r}}{r} \tag{4.2.7}$$

where a is the distance at which the atmosphere of the ion begins. Substituting (4.2.7) in (4.2.6), and the result in (4.2.3), we obtain for the force acting on a spherical shell around the j-ion

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[1] Tentative calculations have shown that this approximation will not affect the limiting law for small concentrations and that the terms thus neglected (of the order $c \log c$) are in general of minor importance. In the case of diffusion, these terms vanish in the absence of a diffusion-potential, like the first ($\sqrt{c}$) terms in (4.2.14) and may be considered as corrections to the latter.

[2] It may appear inconsequent to retain the e^2 term in (4.2.6) and drop the corresponding term in the approximation (4.2.7) for the potential. We have, however, carried through the derivation using the next approximation for the potential given by LaMer and Mason: J. Am. Chem. Soc., 49, 420 (1927), and the final result differs from the one obtained here only by a term of the order of concentration to the first power. Furthermore, it has a small numerical coefficient, and vanishes for a symmetrical electrolyte.

$$\mathbf{F}\,dr = 4\pi\, r^2 \left\{ \frac{-e_j\, e_\sigma}{D\,k\,T} \frac{e^{\kappa a}}{1+\kappa a} \frac{e^{-\kappa r}}{r} + \frac{1}{2} \left(\frac{e_j\, e_\sigma}{DkT} \frac{e^{\kappa a}}{1+\kappa a} \right)^2 \frac{e^{-2\kappa r}}{r^2} \right\} n_\sigma\, \mathbf{k}_\sigma\, dr$$

$$= 4\pi\,(-\,A_1\, r\, e^{-\kappa r} + A_2\, e^{-2\kappa r})\; dr.$$

If we now apply Stokes' formula (4.2.4), this force is seen to give a velocity

$$d\mathbf{v}_j = \frac{\mathbf{F}\,dr}{6\pi\eta r} = \frac{2}{3\eta} \left(-\,A_1\, e^{-\kappa r} + A_2 \frac{e^{-2\kappa r}}{r} \right) dr \qquad (4.2.8)$$

to the shell and the ion at its centre. In order to obtain the total velocity produced by the entire atmosphere of the ion, we simply integrate (4.2.8), whence

$$\Delta\mathbf{v}_j = \frac{2}{3\eta} \int_a^\infty \left\{ -A_1\, e^{-\kappa r} + A_2 \frac{e^{-2\kappa r}}{r} \right\} dr$$

$$= \frac{2}{3\eta} \left\{ -\,A_1 \frac{e^{-\kappa a}}{\kappa} + A_2 \mathrm{Ei}\,(2\,\kappa\, a) \right\} \qquad (4.2.9)$$

where $\mathrm{Ei}(x)$ is the exponential integral function

$$\mathrm{Ei}(x) = \int_x^\infty e^{-t} \frac{dt}{t} = -0.5772 - \log x + x - \frac{x^2}{2.2!} + \dots.$$

If we replace the constants of (4.2.9), we obtain the electrophoretic correction to the velocity

$$\Delta\mathbf{v}_j = -\,\frac{2}{3\eta} \frac{e_j e_\sigma n_\sigma \mathbf{k}_\sigma}{DkT\; \kappa(1 + \kappa a)} + \frac{1}{3\eta} \left(\frac{e_j e_\sigma}{DkT} \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 n_\sigma\, \mathbf{k}_\sigma\, \mathrm{Ei}(2\,\kappa a). \qquad (4.2.10)$$

For an electrical force $\mathbf{k}_i = \mathbf{E}\, e_i$, and κa small, the first term becomes

$$-\mathbf{E}\, e_j\, \kappa / 6\pi\eta \qquad (4.2.11)$$

which is Onsager's result.

Next, we shall see how the electrophoretic correction (4.2.10) affects the diffusion of a simple electrolyte ($s = 2$) where $\mathbf{k}_j = \mathbf{v}/\omega_j$, if $\mathbf{v}$ is the net velocity of diffusion. The velocity correction becomes

$$\Delta\mathbf{v}_j = -\,\frac{2}{3\eta} \left(\frac{n_1 e_1}{\omega_1} + \frac{n_2 e_2}{\omega_2} \right) \frac{e_j \mathbf{v}}{DkT} \frac{1}{\kappa\,(1 + \kappa a)} +$$

$$\frac{1}{3\eta} \left(\frac{n_1 e_1^2}{\omega_1} + \frac{n_2 e_2^2}{\omega_2} \right) \frac{\mathbf{v}\; e_j^2}{(DkT)^2}\, \varphi(\kappa a) \qquad (4.2.12)$$

where

$$\varphi(\kappa a) = e^{2\kappa a}\, \mathrm{Ei}(2\,\kappa a)/(1 + \kappa a)^2.$$

The corresponding force is, per unit volume

$$\sum_j n_j \Delta\mathbf{v}_j / \omega_j\,.$$

To evaluate this sum, we substitute (4.2.12), carry out the summation and use the following relations

$$n_1 e_1 + n_2 e_2 = 0 \tag{4.2.13a}$$

$$\bar{\rho} = \frac{n_1 e_1^2/\omega_1 + n_2 e_2^2/\omega_2}{n_1 e_1^2 + n_2 e_2^2} \tag{4.2.13b}$$

$$\kappa^2 = \frac{4\pi}{DkT}(n_1 e_1^2 + n_2 e_2^2). \tag{4.2.13c}$$

Then

$$\sum_j n_j \, \Delta \mathbf{v}_j/\omega_j = -\frac{\mathbf{v}}{6\,\pi\eta}\,\frac{n_1 n_2}{n_1 + n_2}\,\frac{\kappa}{1 + \kappa a}\,(\rho_1 - \rho_2)^2 + \frac{(\bar{\rho})^2\,\mathbf{v}\,\kappa^4}{48\pi^2\,\eta}\,\varphi(\kappa a).$$

The average force per ion is accordingly

$$\frac{\sum\limits_j n_j \, \Delta \mathbf{v}_j/\omega_j}{n_1 + n_2} =$$

$$= \mathbf{v}\left(\frac{-1}{6\pi\eta}\,\frac{z_1 z_2}{(z_1 + z_2)^2}\,\frac{\kappa}{(1 + \kappa a)}\,(\rho_1 - \rho_2)^2 + \frac{(\bar{\rho})^2}{48\pi^2\eta}\,\frac{\kappa^4\,\varphi(\kappa a)}{n_1 + n_2}\right) \tag{4.2.14}$$

where we have introduced the valences $z_1 = |e_1|/\epsilon$ and $z_2 = |e_2|/\epsilon$ in the first term. The correction is, first of all, proportional to the velocity, (i.e. to the acting force, which in the case of diffusion is the gradient of the total chemical potential μ. This point will be discussed in detail in §4.13). The two terms of (4.2.14) are of opposite sign. The first term depends on the square root of the concentration and on the square of the *difference* in mobility of the two ions present. The second term is of the order $c \log c$ (c = concentration) and otherwise depends only on the average (with respect to ionic strength) of the mobilities.

We shall need for a later discussion the contribution to diffusion due to electrophoresis. The corresponding number of ions per second crossing a unit area perpendicular to the direction of diffusion equals

$$\Delta J_j = n_j \, \Delta \mathbf{v}_j =$$

$$= \left(-\frac{2}{3\eta}\,\frac{n_j\,e_j\,n_\sigma\,e_\sigma}{DkT\;\kappa(1 + \kappa a)} + \frac{1}{3\eta}\,\frac{n_\sigma\,e_\sigma^2\,n_j\,e_j^2\,\varphi(\kappa a)}{(DkT)^2}\right)\mathbf{k}_\sigma. \tag{4.2.15}$$

If we write $\Delta J_j = \Delta\Omega_{j\sigma}\mathbf{k}_\sigma$, then

$$\Delta\Omega_{ji} = \frac{\partial \Delta J_j}{\partial\,\mathbf{k}_i} =$$

$$= -\frac{2}{3\eta}\,\frac{n_j\,e_j\,n_i\,e_i}{DkT\;\kappa(1 + \kappa a)} + \frac{1}{3\eta}\,\frac{n_i\,e_i^2\,n_j\,e_j^2\,\varphi(\kappa a)}{(DkT)^2}. \tag{4.2.16}$$

This result applies to an arbitrary mixture of ions. We note that $\Delta\Omega_{ji}$ is symmetrical as required (cf. §4.15).

For a simple electrolyte, we have, using (4.2.13),

$$\Delta\Omega_{11} = -\frac{n_1 z_1 \kappa}{6\pi\eta\,(1+\kappa a)\,(z_1+z_2)} + \frac{z_1^2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta(z_1+z_2)^2} \tag{4.2.17a}$$

$$\Delta\Omega_{12} = \frac{n_1 z_1 \kappa}{6\pi\eta\,(1+\kappa a)\,(z_1+z_2)} + \frac{z_1 z_2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta(z_1+z_2)^2} = \Delta\Omega_{21} \tag{4.2.17b}$$

$$\Delta\Omega_{22} = -\frac{n_1 z_1 \kappa}{6\pi\eta\,(1+\kappa a)\,(z_1+z_2)} + \frac{z_2^2 \kappa^4 \varphi(\kappa a)}{48\pi^2 \eta(z_2+z_2)^2} \tag{4.2.17c}$$

4.3. *Specialization of the Fundamental Equations for Ionic Forces.*

In adapting the general equation of continuity (2.5.7) to the conductance diffusion problem, we naturally consider the special case where no velocity gradient is present. Accordingly, the velocity terms drop out and furthermore, ψ'_j and f_{ji} no longer depend on location, so that we simply have to deal with functions of the form $\psi'_j\,(\mathbf{r}_{21})$. Then (2.5.7) becomes

$$\begin{aligned} &\omega_i\,(\mathbf{K}_i, \operatorname{grad}_2 f^\circ_{ji}(r)) + \omega_j\,(\mathbf{K}_j, \operatorname{grad}_1 f^\circ_{ij}(r)) \\ &- e_i\,\omega_i\,n_i\,n_j\,\Delta_2\psi'_j(\mathbf{r}_{21}) - e_j\,\omega_j\,n_i\,n_j\,\Delta_1\psi'_i(-\mathbf{r}_{21}) \\ &- \omega_i\,k\,T\,\Delta_2 f'_{ji}(\mathbf{r}_{21}) - \omega_j\,k\,T\,\Delta_1 f'_{ij}(-\mathbf{r}_{21}) = 0. \end{aligned} \tag{4.3.1}$$

The differential operators in the above equation may all be reduced to differentiation with respect to $q^l = q^l_{21}$ ($l = 1, 2,$ and 3) since there are no longer functions of $\mathbf{r}_1$ or $\mathbf{r}_2$ present. Since $q_{21} = q_2 - q_1$ and $f^\circ_{ji}(r) = f^\circ_{ij}(r)$, we have

$$\operatorname{grad}_1 f^\circ_{ij}\,(r) = -\operatorname{grad}_2 f^\circ_{ij}\,(r) = -\operatorname{grad} f^\circ_{ji}\,(r)$$

and

$$\Delta_2 = \Delta_1 = \Delta_{21} = \Delta.$$

If we now write $\mathbf{r}$ for $\mathbf{r}_{21}$ and $-\mathbf{r}$ for $\mathbf{r}_{12}$, the subscripts 1, 2 may be dropped and we obtain

$$\begin{aligned} &\omega_i\,(\mathbf{K}_i, \operatorname{grad} f^\circ_{ji}\,(r)) - \omega_j\,(\mathbf{K}_j, \operatorname{grad} f^\circ_{ji}\,(r)) \\ &- e_i\,\omega_i\,n_i\,n_j\,\Delta\psi'_j\,(\mathbf{r}) - e_j\,\omega_j\,n_i\,n_j\,\Delta\psi'_i\,(-\mathbf{r}) \\ &- \omega_i\,k\,T\,\Delta f'_{ji}\,(\mathbf{r}) - \omega_j\,k\,T\,\Delta f'_{ij}\,(-\mathbf{r}) = 0. \end{aligned} \tag{4.3.2}$$

We defined ψ'_j and f'_{ji} in §2.5 as the asymmetric additions to potential and distribution produced by any agency which destroyed the symmetry of the ionic atmospheres. They were assumed small with respect to the functions ψ°_j and f'_{ji} characteristic of the solution in the unperturbed state. Now here we shall consider the effects due to a force $\mathbf{k}$ and shall assume ψ°_j and f'_{ji} proportional to this force. For the migration problem this means, then, that we limit the discussion to conductance and diffusion under ordinary field strengths and concentration gradients, where proportionality applies.[1] Consequently, the general form of the addition functions must be

$$(\mathbf{r}, \mathbf{k})\;R(r) \tag{4.3.3}$$

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[1] Arguments based on this limitation were first used in connection with the Debye-Hückel theory by Redlich: Physik. Z., 26, 199 (1925).

where $R(r)$ is a function of the scalar distance r and where $(\mathbf{r}, \mathbf{k})$, linear in $\mathbf{k}$ as required, gives the dependence on direction. Functions of this type must satisfy the following symmetry conditions

$$\varphi(-\mathbf{r}) = -\varphi(\mathbf{r}), \text{ i.e.,}$$

$$\psi'_i(-\mathbf{r}) = -\psi'_i(\mathbf{r})$$

$$f'_{ji}(-\mathbf{r}) = -f'_{ji}(\mathbf{r}) = -f'_{ij}(-\mathbf{r});\, f'_{jj} = 0. \tag{4.3.4}$$

If we substitute these in (4.3.2) and recall that $f'_{ij}(-\mathbf{r}) = f'_{ji}(\mathbf{r})$, the resulting equation will contain only functions of r:

$$\omega_i(\mathbf{k}_i, \operatorname{grad} f^\circ_{ji}) - \omega_j(\mathbf{k}_j, \operatorname{grad} f^\circ_{ji}) - e_i\,\omega_i\,n_i\,n_j\,\Delta\psi'_j(\mathbf{r})$$
$$+ e_j\,\omega_j\,n_i\,n_j\,\Delta\psi'_i(\mathbf{r}) - (\omega_i + \omega_j)\,kT\,\Delta f'_{ji}(\mathbf{r}) = 0. \tag{4.3.5}$$

This may be simplified further with no actual loss of generality by the assumption that the forces $\mathbf{k}_i$, $\mathbf{k}_j$ have components k_i, k_j only in the x-direction; then

$$(\mathbf{k}, \operatorname{grad} f^\circ_{ji}) = k\frac{\partial f^\circ_{ji}}{\partial x}$$

and (4.3.5) becomes

$$(\omega_i\,k_i - \omega_j\,k_j)\frac{\partial f^\circ_{ji}}{\partial x} - e_i\,\omega_i\,n_i\,n_j\,\Delta\psi'_j +$$
$$e_j\,\omega_j\,n_i\,n_j\,\Delta\psi'_i - (\omega_i + \omega_j)\,kT\,\Delta f'_{ji} = 0. \tag{4.3.6}$$

In view of the relations (4.3.4), there are $\frac{1}{2}\,s(s-1)$ independent distribution functions f'_{ji}; (4.3.6) accordingly is a system of $\frac{1}{2}\,s(s-1)$ differential equations connecting these with the s potentials.

4.4. *Differential Equations for the Potentials.*

By means of the s Poisson equations

$$\Delta\psi'_j = -\frac{4\pi}{D}\sum_i \frac{e_i}{n_j} f'_{ji} \tag{4.4.1}$$

the system (4.3.6) is made complete, and we may now eliminate the distribution functions from (4.3.6) by means of (4.4.1)

$$\Delta\Delta\psi'_j - \frac{4\pi}{DkT}\sum_i \frac{n_i\,e_i^2\,\omega_i}{\omega_i + \omega_j}\Delta\psi'_j + \frac{4\pi}{DkT}\sum_i \frac{n_i\,e_i\,e_j\,\omega_j}{\omega_i + \omega_j}\Delta\psi'_i =$$
$$= -\frac{4\pi}{DkT}\sum_i \frac{\omega_i\,k_i - \omega_j\,k_j}{\omega_i + \omega_j}\,\frac{e_i}{n_j}\,\frac{\partial f^\circ_{ji}}{\partial x}$$
$$= \frac{4\pi}{(DkT)^2}\sum_i \frac{\omega_i\,k_i - \omega_j\,k_j}{\omega_i + \omega_j}\,n_i\,e_i^2\,e_j\,\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) \tag{4.4.2}$$

on substituting the value of f°_{ji} given by (2.4.11).

It has been pointed out previously[1] that by multiplying (4.4.2) by $n_j e_j$ and summing over j that

$$\sum_j n_j e_j \Delta\Delta\psi'_j = 0, \tag{4.4.3}$$

and since ψ'_j and $\Delta\psi'_j$ must vanish for $r = \infty$ and always remain finite,

$$\sum_i n_j e_j \Delta\psi'_j = 0.$$

If we write i for j in the last equation and multiply by $4\pi e_j/DkT$, we obtain

$$\frac{4\pi}{DkT}\sum_i n_i e_i e_j \Delta\psi'_i = 0$$

which may be subtracted from (4.4.2). From the resulting set of coefficients, when we later introduce matrix formulation, we shall obtain the same symmetrical matrix K that appeared in the viscosity problem. We shall then be able to utilize our knowledge of the properties of K in our present problem. After subtraction, we have

$$\begin{aligned}\Delta\Delta\psi'_j - \frac{4\pi}{DkT}\sum_i \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j}\Delta\psi'_j - \frac{4\pi}{DkT}\sum_i \frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j}\Delta\psi'_i = \\ = \frac{4\pi}{(DkT)^2}\sum_i \frac{\omega_i k_i - \omega_j k_j}{\omega_i + \omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x}\left(\frac{e^{-r\kappa}}{r}\right)\end{aligned} \tag{4.4.4}$$

as the differential equations determining the potentials ψ'_j.

4.5. *Matrix Formulation and Solution.*

The equations (4.4.4) can be written compactly by introducing matrix notation and s-dimensional vectors in "ion-space." Again we shall find that in this form, the equations are readily solved explicitly for the general case of s ions. Let the elements of a matrix C be defined by

$$c_{ji} = \frac{4\pi}{DkT}\left(\frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_\sigma + \omega_j}\delta_{ji} + \frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j}\right) \tag{4.5.1}$$

and the components h_j of a vector $\mathbf{h}$ by

$$h_j = \frac{4\pi}{(DkT)^2}\left(\frac{k_\sigma \omega_\sigma - k_j \omega_j}{\omega_\sigma + \omega_j} n_\sigma e_\sigma^2 e_j\right). \tag{4.5.2}$$

(Greek indices always imply summation over $\sigma = 1, 2, \ldots, s$). Then we may write (4.4.4) as

$$\Delta(\Delta\delta_{j\tau} - c_{j\tau})\psi'_\tau = h_j \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right)$$

which is the component form of the operator equation

$$\Delta(\Delta - \mathbf{C})\mathbf{y} = \mathbf{h}\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right) \tag{4.5.3}$$

if $\mathbf{y}$ is a vector with components ψ'_j.

---

[1] Onsager: Loc. cit., p. 284.

The matrix C is made symmetrical by the following transformation:

$$K = P\,C\,P^{-1}$$

$$p_{ji} = \delta_{ji}\sqrt{n_j\,\omega_j}$$

$$k_{ji} = \frac{4\pi}{DkT}\left(\frac{n_\sigma\,e_\sigma^2\,\omega_\sigma}{\omega_\sigma + \omega_j}\,\delta_{ji} + \frac{e_i\,e_j\sqrt{n_i\,n_j\,\omega_i\,\omega_j}}{\omega_i + \omega_j}\right) \qquad (4.5.4)$$

The result K of this transformation is the same matrix K that appeared in the viscosity problem. We have shown that its characteristic numbers $\alpha_1, \ldots, \alpha_s$ are all positive (3.8.4) and that $\alpha_1 = \kappa^2$ (3.8.6) is the greatest of them. Also the eigenvector $\mathbf{l}_1$ corresponding to α_1 is given by (3.8.5)

$$l_{1j} = e_j\sqrt{n_j/\omega_j}\,(n_\sigma\,e_\sigma^2/\omega_\sigma)^{-1/2}. \qquad (4.5.5)$$

Since, by (4.5.1), the matrix C has the same characteristic numbers as K, all real $\geqslant 0$; the matrices G satisfying

$$G^2 = C,\ g_{j\sigma}\,g_{\sigma i} = c_{ji} \qquad (4.5.6)$$

will all be real. One of these will have all characteristic numbers $\sqrt{\alpha_1}, \ldots, \sqrt{\alpha_s}$ positive: we shall represent this particular one simply by G.

Now if $\varphi(r, \gamma)$ is a solution of

$$\Delta\,(\Delta - \gamma^2)\,\varphi(r, \gamma) = \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right), \qquad (4.5.7)$$

then in accordance with the definitions of functions of matrices,[1]

$$\Delta\,(\Delta - \mathbf{G}^2)\,\varphi(r, \mathbf{G}) = \frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right)\mathbf{1} \qquad (4.5.8)$$

so that $\Delta(\Delta - \mathbf{G}^2)\,\varphi(r, \mathbf{G})$ operating on $\mathbf{h}$ is the same as multiplying $\mathbf{h}$ by the scalar function $\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right)$. Then

$$\mathbf{y} = \varphi(r, \mathbf{G})\,\mathbf{h} \qquad (4.5.9)$$

is a solution of (4.5.3).

We now proceed to find the solution of (4.5.7) which satisfies the boundary conditions that the potential must vanish for $r = \infty$ and must remain finite for all values of r. (The boundary conditions for potentials have been discussed in detail in a preceding section, §3.5.) A particular solution of (4.5.7) is

$$\varphi\,(r, \gamma) = \frac{1}{\kappa^2(\kappa^2 - \gamma^2)}\,\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{r}\right),$$

to which we add the general solution of the homogeneous equation. According to (4.3.3), we only have to consider functions of the type $xR(r)$, or what amount to the same, of the form $\partial R(r)/\partial x$. With this restriction, the most general solution of (4.5.7) is

$$\varphi\,(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2}\,\frac{\partial}{\partial x}\left(\frac{e^{-\kappa r}}{\kappa^2\,r} + A_1\,\frac{e^{\gamma r}}{r} + A_2\,\frac{e^{-\gamma r}}{r} + A_3 r^2 + A_4\,\frac{1}{r}\right).$$

---

[1] See also footnote following (3.5.7a).

In order that φ vanish for $r = \infty$,

$$A_1 = A_3 = 0,$$

and in order that $\Delta\varphi$ remain finite at $r = 0$,

$$A_2 = -1/\gamma^2.$$

Then, on substituting these constants, we see that

$$A_4 = \frac{1}{\gamma^2} - \frac{1}{\kappa^2}$$

in order that φ remain finite at $r = 0$. Our solution is accordingly

$$\varphi\,(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2}\,\frac{\partial}{\partial x}\left(\frac{1 - e^{-\gamma r}}{\gamma^2\, r} - \frac{1 - e^{-\kappa r}}{\kappa^2 r}\right). \qquad (4.5.10)$$

We are now able to write the solution of the matrix equation (4.5.3)

$$\mathbf{y} = \varphi(r, \mathbf{G})\,\mathbf{h}$$

$$\psi'_j = \varphi(r, G)_{j\sigma}\, h_\sigma \qquad (4.5.11)$$

which satisfies the boundary conditions of the problem since G has all characteristic numbers positive. We also assert that this solution is unique; for proof, we refer to the entirely parallel case in §3.5.

In the conductance-diffusion problem, we shall be particularly interested in the value of the field strength $-\text{grad}\ \psi_j'$ for $r = 0$. By expanding the exponentials in power series and carrying out the differentiation with respect to x indicated in (4.5.10), we obtain

$$\varphi(r, \gamma) = \frac{1}{\kappa^2 - \gamma^2}\left(\frac{\gamma - \kappa}{3}\,x + \frac{\kappa^2 - \gamma^2}{8}\,rx + O(r^2)\right)$$

and

$$\frac{\partial\,\varphi\,(r, \gamma)}{\partial x} = \frac{1}{\kappa^2 - \gamma^2}\left(\frac{\gamma - \kappa}{3} + \frac{\kappa^2 - \gamma^2}{8}\,r + \frac{\kappa^2 - \gamma^2}{8}\,\frac{x^2}{r} + O(r^2)\right).$$

In the limit $r = 0$ this becomes

$$\left(\frac{\partial\varphi}{\partial x}\right)_{r = 0} = -\frac{1}{3}\,(\kappa + \gamma)^{-1}$$

so that

$$\text{grad}_x\, \psi'_j\,(0) = -\tfrac{1}{3}\,\left\{(\kappa + G)^{-1}\right\}_{j\sigma} h_\sigma. \qquad (4.5.12)$$

4.6. *Simplification of Matrix Solution.*

The rather complicated ion-vector $\mathbf{h}$ can now be simplified if we write

$$h_j = \frac{1}{DkT} b_{j\sigma}\, k_\sigma \qquad (4.6.1)$$

and identify by comparison with (4.5.2) the elements b_{ji} to be

$$b_{ji} = \frac{4\pi}{DkT}\left(\frac{n_i\, e_i^2\, \omega_i}{\omega_i + \omega_j}\, e_j - \delta_{ji}\, \frac{n_\sigma\, e_\sigma{}^2\, \omega_j}{\omega_j + \omega_\sigma}\, e_j\right).$$

In the last term we may write either i or j as subscript, due to the coefficient δ_{ji}; then

$$b_{ji} = \frac{4\pi}{DkT}\left(\frac{n_i\, e_i\, e_j\, \omega_i}{\omega_i + \omega_j} + \delta_{ji}\, \frac{n_\sigma\, e_\sigma^{\,2}\, \omega_\sigma}{\omega_j + \omega_\sigma} - \delta_{ji}\, n_\sigma\, e_\sigma^{\,2}\right) e_i$$

$$= (c_{ji} - \delta_{ji}\, \kappa^2)\, e_i. \tag{4.6.2}$$

Substituting this value in (4.6.1),

$$h_j = \frac{1}{DkT}\, (C - \kappa^2)_{j\sigma}\, e_\sigma\, k_\sigma$$

or

$$\mathbf{h} = \frac{1}{DkT}\, (\mathbf{C} - \kappa^2)\, \mathbf{m}, \tag{4.6.3}$$

where $\mathbf{m}$ is a vector with components $e_j\, k_j$. The value of $\text{grad}_x\, \psi'_j(0)$ given by (4.5.12) now becomes

$$\text{grad}_x\, \psi'_j(0) = \frac{1}{3\, DkT}\left\{ (\kappa + C^{1/2})^{-1} \right\}_{j\tau} (\kappa^2 - C)_{\tau\sigma}\, e_\sigma\, k_\sigma$$

$$= \frac{1}{3\, DkT}\, (\kappa - C^{1/2})_{j\sigma}\, e_\sigma\, k_\sigma$$

$$= \frac{1}{3\, DkT}\, \frac{\kappa}{\sqrt{n_j\, \omega_j}}\, (1 - \kappa^{-1} K^{1/2})_{j\sigma} \sqrt{n_\sigma\, \omega_\sigma}\, e_\sigma\, k_\sigma. \tag{4.6.4}$$

This result for the field strength produced by the asymmetry of the ionic atmosphere involves the root $G = C^{1/2}$ of the matrix C. There are several ways in which the numerical computation may be made. One method, which is always applicable and in most cases convenient, proceeds by expansion of the function $f(K) = (1 - \kappa^{-1} K^{1/2})$ in a Taylor series. The series obtained will ordinarily converge rapidly except for the terms in the sum corresponding to the maximum characteristic number $\alpha_1 = \kappa^2$. This inconvenient behavior of the series may be correct by any one of several devices; we prefer to use the same one which served in the viscosity problem.

We have explicitly the eigenvector $\mathbf{l}_1$ (4.5.5). An eigenvector $\mathbf{l}_j$ corresponding to a characteristic number α_j of a matrix A is by definition a vector such that

$$\mathbf{A}\, \mathbf{l}_j = \alpha_j\, \mathbf{l}_j,$$

i.e., operating on $\mathbf{l}_j$ with the tensor $\mathbf{A}$ is equivalent to multiplying by the scalar α_j. Consequently $(f(\mathbf{C}), \mathbf{l}_1)$ vanishes, and we may add to the vector $\mathbf{t}$ in (4.6.4) with the components $t_i = e_i k_i \sqrt{n_i\, \omega_i}$ any multiple of $\mathbf{l}_1$, without changing the value of the product. The component of $\mathbf{t}$ "parallel" to $\mathbf{l}_1$ is given by

$$(\mathbf{l}_1, \mathbf{t})\, l_{1j} = e_j \sqrt{\frac{n_j}{\omega_j}}\, \frac{n_\sigma\, e_\sigma^{\,2}\, k_\sigma}{n_\tau\, e_\tau^{\,2}/\omega_\tau}$$

and the component "perpendicular" to $\mathbf{l}_1$ is then given by

$$t_i - (\mathbf{l}_1, \mathbf{t})\, l_{1i} = \sqrt{n_i\,\omega_i}\, e_i\, k_i - \sqrt{\frac{n_i}{\omega_i}}\, \frac{n_\sigma\, e_\sigma^2\, k_\sigma}{n_\tau\, e_\tau^2\, \rho_\tau}\, e_i = p_i. \tag{4.6.5}$$

The vector $\mathbf{p}$ thus determined may then replace $\mathbf{t}$ in (4.6.4); but by construction, $\mathbf{p}$ is orthogonal to $\mathbf{l}_1$, so that the terms corresponding to $\alpha_1 = \kappa^2$ will never appear when the sum is computed. With this substitution, (4.6.4) becomes

$$\mathrm{grad}_x\, \psi'_j\,(0) = \frac{\kappa}{3\,DkT}\, \frac{1}{\sqrt{n_j\,\omega_j}}\, (1 - \kappa^{-1}\, K^{1/2})_{j\sigma}\, p_\sigma. \tag{4.6.6}$$

The series expansion is readily obtained by considering $f(z) = 1 - \sqrt{z}$. By substituting $z = t + 1/2$, we have the following identities:

$$1 - \sqrt{z} = (\sqrt{2} - \sqrt{1 + 2t})\, 2^{-1/2}$$

$$(1 + 2t)^{1/2} = \sum_{n=0}^{\infty} \binom{1/2}{n} (2t)^n$$

$$1 - \sqrt{z} = 2^{-1/2}\Big\{\sqrt{2} - \sum_{n=0}^{\infty} \binom{1/2}{n} (2t)^n\Big\}$$

$$= \sum_{n=0}^{\infty} c_n\, (2z - 1)^n \tag{4.6.7}$$

where

$$c_0 = \tfrac{1}{2}\,(2 - \sqrt{2});\; c_n = -\,\frac{\sqrt{2}}{2} \binom{1/2}{n} \text{ for } n \geq 1. \tag{4.6.8}$$

$$\begin{array}{llll}
c_0 = & 0.2929 & c_3 = & -0.0442 \\
c_1 = & -0.3536 & c_4 = & 0.0276 \\
c_2 = & 0.0884 & c_5 = & -0.0193
\end{array}$$

Then

$$f(\mathbf{K})\,\mathbf{p} = \sum_{n=0}^{\infty} c_n\, (2\kappa^{-2}\mathbf{K} - \mathbf{1})^n\, \mathbf{p}. \tag{4.6.9}$$

The vector $\mathbf{p}$ includes the acting force. In order to show this fact explicitly, we write

$$p_i = F_{i\sigma} k_\sigma \tag{4.6.10}$$

and identify F_{ji} to be

$$F_{ji} = \frac{\partial p_j}{\partial k_i} = \sqrt{n_j\,\omega_j}\, e_j\, \delta_{ji} - e_j \sqrt{\frac{n_j}{\omega_j}}\, \frac{n_i\, e_i^2}{n_\tau\, e_\tau^2\, \rho_\tau}$$

$$= e_j \sqrt{n_j\,\omega_j} \left(\delta_{ji} - \frac{n_i\, e_i^2\, \rho_j}{n_\tau\, e_\tau^2\, \rho_\tau} \right). \tag{4.6.11}$$

Substituting these into (4.6.9) and the result into (4.6.6), we finally obtain

$$\mathrm{grad}_x\, \psi'_j\,(0) = \frac{\kappa}{3\,DkT}\, \frac{1}{\sqrt{n_j\,\omega_j}} \sum_{n=0}^{\infty} c_n\, (2\,\kappa^{-2}\, K - 1)^n{}_{j\sigma}\, F_{\sigma\tau}\, k_\tau. \tag{4.6.12}$$

4.7. *Conversion to Practical Units.*

In order to compare with experimental results, we shall need formula (4.6.12) expressed in practical units. We recall the transformations made in the viscosity problem:

$$\Gamma_i = m_i z_i^2 = \frac{1000}{N\epsilon^2} n_i e_i^2 \tag{4.7.1}$$

$$\mu_i = \frac{\Gamma_i}{\Gamma} = \frac{n_i e_i^2}{n_\sigma e_\sigma^2} \tag{4.7.2}$$

$$\kappa^2 = \frac{N\epsilon^2}{1000} \frac{4\pi}{DkT} \Gamma \tag{4.7.3}$$

$$\omega_j = \frac{300}{\epsilon} \frac{\bar{u}^\circ{}_j}{z_j} = \frac{300\,\Lambda^\circ{}_j}{96\,500\,\epsilon\, z_j} \tag{4.7.4}$$

$$M\,K\,M^{-1} = G', \;\; m_{ji} = \delta_{ji}\, e_j \sqrt{n_j \omega_j} \tag{4.7.5}$$

$$h_{ij} = h'_{ji} = \frac{g'_{ji}}{\kappa^2} = \delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_j \frac{\omega_j}{\omega_j + \omega_i}\cdot \tag{4.7.6}$$

In the migration problem, it will be more convenient to use the matrix H instead of its transposed H'; we have

$$M^{-1}\,K\,M = G = \kappa^2 H$$

$$h_{ji} = \frac{g_{ji}}{\kappa^2} = \delta_{ji} \sum_i \mu_i \frac{\omega_i}{\omega_i + \omega_j} + \mu_i \frac{\omega_i}{\omega_j + \omega_i}\cdot \tag{4.7.7}$$

The matrix H has pure numbers as its elements and so has $(1 - \kappa^{-1} G^{1/2}) = (1 - H^{1/2})$. The matrix H is not symmetrical; in this case, the eigenvectors $\mathbf{x}_p$ and their adjoints $\mathbf{x}^*{}_p$ are[1] defined by the following relations .

$$\mathbf{H}'\,\mathbf{x}^*{}_p = \zeta_p \mathbf{x}^*{}_p;\, \mathbf{H}\mathbf{x}_p = \zeta_p \mathbf{x}_p;\, (\mathbf{x}_p, \mathbf{x}^*{}_q) = \delta_{pq} \tag{4.7.8}$$

where $\zeta_p = \alpha_p/\kappa^2$ are the characteristic numbers of H. The eigenvectors of H are readily connected with those of K by the following transformations:

$$\mathbf{K}\,\mathbf{l}_j = \alpha_j\,\mathbf{l}_j = \kappa^2\,\mathbf{M}\,\mathbf{H}\,\mathbf{M}^{-1}\,\mathbf{l}_j,$$

whence

$$\mathbf{H}\,\mathbf{M}^{-1}\,\mathbf{l}_j = \zeta_j\,\mathbf{M}^{-1}\,\mathbf{l}_j \text{ and } \mathbf{x}_j = \mathbf{M}^{-1}\,\mathbf{l}_j. \tag{4.7.9a}$$

Likewise

$$\mathbf{K}'\,\mathbf{l}_j = \alpha_j\,\mathbf{l}_j = \kappa^2\,\mathbf{M}^{-1}\,\mathbf{H}'\,\mathbf{M}\,\mathbf{l}_j,$$

whence

$$\mathbf{H}'\,\mathbf{M}\,\mathbf{l}_j = \zeta_j\,\mathbf{M}\,\mathbf{l}_j \text{ and } \mathbf{x}^*{}_j = \mathbf{M}\,\mathbf{l}_j. \tag{4.7.9b}$$

For the case of conduction without diffusion, the forces k_j equal Xe_j, where X is the applied electric field. We substitute this in our general result (4.6.6) for $\text{grad}_x\, \psi'_j\,(0) = -\Delta X_j$ and obtain

---

[1] A trivial ambiguity remains in this definition, inasmuch as $\mathbf{x}_p$ may be multiplied by a scalar λ_p while $\mathbf{x}^*{}_p$ is divided by the same factor. In certain special cases, the ambiguity is greater, but still trivial as far as our purposes are concerned.

$$
\begin{aligned}
-\frac{\Delta X_j}{X} &= \frac{\kappa}{3DkT}\frac{1}{\sqrt{n_j\,\omega_j}}\left\{M\,(1 - H^{1/2})\,M^{-1}\right\}_{j\sigma} F_{\sigma\tau}\,e_\tau \\
&= \frac{\kappa}{3DkT}e_j\,(1 - H^{1/2})_{j\sigma}\left(\delta_{\tau\sigma} - \frac{n_\tau\,e_\tau^2\,\rho_\sigma}{n_\pi\,e_\pi^2\,\rho_\pi}\right)e_\tau \\
&= \frac{\epsilon^3}{3}\sqrt{\frac{N\,\pi}{250\,k^3}}\frac{\Gamma^{1/2}}{(DT)^{3/2}}z'_j\,(1 - H^{1/2})_{j\sigma}\,r_\sigma
\end{aligned}
\tag{4.7.10}
$$

where **r** is a vector defined by

$$
r_i = \left(\delta_{i\tau} - \frac{n_\tau\,e_\tau^2\,\rho_i}{n_\pi\,e_\pi^2\,\rho_\pi}\right)z'_\tau = z'_i - \frac{z'_\tau\,\mu_\tau}{\mu_\pi\,z_\pi/\Lambda^\circ_\pi}\frac{z_i}{\Lambda^\circ_i}\,. \tag{4.7.11}
$$

The primes on the valences z'_i mean that they must carry the sign of the corresponding ionic charge. We note that the second term of r_i vanishes for a symmetrical electrolyte ($z'_\tau\,\mu_\tau = 0$); in this case, the vector **t** of (4.6.5) is already orthogonal to the eigenvector $\mathbf{l}_1$. For convenience in numerical computation, we define vectors $\mathbf{r}^{(n)}$ by means of the recursion formula

$$
r_j^{(n)} = (2H - 1)_{j\sigma}\,r^{(n-1)}_\sigma\,;\ r^{(0)}_j = r_j. \tag{4.7.12}
$$

Then our formula becomes, on substituting numerical values for the universal constants ($N = 6.06 \times 10^{23}$; $k = 1.371 \times 10^{-16}$ erg/1°; $\epsilon = 4.774 \times 10^{-10}$ e.s.u.) in (4.7.10),

$$
\frac{\Delta X_j}{X} = 1.971 \times 10^6\frac{\Gamma^{1/2}}{(DT)^{3/2}}z'_j\sum_{n=0}^{\infty}c_n\,r_j^{(n)} \tag{4.7.13}
$$

where the coefficients c_n of the series expansion for $(1 - H^{1/2})$ are given by (4.6.8).

4.8. *Conductance in Mixed Electrolytes.*

We are now ready to compute the conductances in a mixture of s species of ions. The net field acting on an ion is $X + \Delta X_j$ where ΔX_j is the added field caused by the finite time of relaxation of the ionic atmosphere. Due to electrophoresis, the velocity v_j of the ion is less than $(X + \Delta X_j)\,e_j\,\omega_j$, which would correspond to the acting force $(X + \Delta X_j)\,e_j$, so that we have for the net velocity

$$
v_j = X\left(e_j\,\omega_j + \frac{\Delta X_j}{X}e_j\,\omega_j - \frac{e_j\,\kappa}{6\,\pi\eta}\right)
$$

on substituting (4.2.11) for the electrophoretic correction. The mobility in electrostatic units is $u_j = |v_j|/X$, and in practical units for a potential gradient of one volt/cm is

$$
\overline{u_j} = \frac{1}{300}\left(|\,e_j\,|\,\omega_j + \frac{\Delta X_j}{X}\,|\,e_j\,|\,\omega_j - \frac{|\,e_j\,|\,\kappa}{6\,\pi\,\eta}\right).
$$

The quantity $|e_j|\omega_j/300$ is the limiting mobility $\overline{u^\circ_j}$ for infinite dilution. Since the equivalent conductance $\Lambda_j = 96500\,\overline{u_j}$, we have

$$
\Lambda_j = \Lambda^\circ_j + \frac{\Delta X_j}{X}\Lambda^\circ_j - \frac{\epsilon^2\,965}{18}\sqrt{\frac{N}{250\pi k}}\,\frac{z_j\,\Gamma^{1/2}}{\eta\,(DT)^{1/2}}\,.
$$

If we now substitute (4.7.13) and evaluate the constants, we obtain for our final result

$$\Lambda_j = \Lambda^\circ_j - \left(\frac{1.971 \times 10^6}{(DT)^{3/2}} \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + \frac{28.98\, z_j}{\eta\, (DT)^{1/2}} \right) \Gamma^{1/2}. \tag{4.8.1}$$

For aqueous solutions at 25°, using Drake, Peirce and Dow's[1] value of the dielectric constant $D = 78.57$ and 0.00895 for the viscosity of water,

$$\Lambda_j = \Lambda^\circ_j - (0.5502\, \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + 21.17\, z_j)\, \Gamma^{1/2}, \tag{4.8.2}$$

and for 18°, using $D = 81.17$ and $\eta = 0.01056$,

$$\Lambda_j = \Lambda^\circ_j - (0.5429\, \Lambda^\circ_j z'_j \sum_{n=0}^{\infty} c_n r_j^{(n)} + 17.85\, z_j)\, \Gamma^{1/2}. \tag{4.8.3}$$

These formulas give the limiting law for the conductance of the *j*-th species of ions in a mixture of *s* different kinds. The electrophoretic correction of course depends only on the square root of the total ionic strength, but the relaxation correction depends also on the mobility ratios and on the ratios $\mu_1, \ldots, \mu_s$ in which the various ions are present. The nature of this dependence will be made clear by considering several numerical examples, although we can already see from (4.5.1) that the "mixture effect" will be greater, the more the mobility ratios deviate from unity.

4.9. *Method of Computation.*

For $s = 2$ or 3, the most convenient method of computation proceeds by (explicit or implicit) evaluation of the characteristic numbers of the matrix H. For $s = 2$, the characteristic numbers are $\zeta_1 = 1$ and $\zeta_2 = q$ (compare (3.8.29) in the viscosity discussion); then $(1 - \zeta_1) = 0$ and $(1 - \mathbf{H}^{1/2})_{j\sigma} r_\sigma$ reduces to $(1 - \sqrt{q})\, r_j$. The result can be written in the form

$$\Lambda_j = \Lambda^\circ_j - \left(\frac{1.971 \times 10^6}{(DT)^{3/2}} \; \frac{q}{1 + \sqrt{q}}\, z_1 z_2 \Lambda^\circ_j - \frac{29.0\, z_j}{\eta\, (DT)^{1/2}} \right) \Gamma^{1/2} \tag{4.9.1}$$

given previously by one of us.

For $s = 3$, H has three characteristic numbers, ζ_j, one of which is unity. In our formula, $\mathbf{r}$ is orthogonal[2] to the eigenvector $\mathbf{x}^*_1$ of $\mathbf{H}'$ because $\mathbf{p}$ of (4.6.5) was constructed orthogonal to the eigenvector $\mathbf{l}_1$ of K. Then by using the properties of the eigenvectors,

$$\begin{aligned}(1 - \mathbf{H}^{1/2})\, \mathbf{r} &= (1 - \mathbf{H}^{1/2}) \left\{ (\mathbf{x}^*_2, \mathbf{r})\, \mathbf{x}_2 + (\mathbf{x}^*_3, \mathbf{r})\, \mathbf{x}_3 \right\} \\ &= (1 - \zeta_2^{1/2})\, (\mathbf{x}^*_2, \mathbf{r})\, \mathbf{x}_2 + (1 - \zeta_3^{1/2})\, (\mathbf{x}^*_3, \mathbf{r})\, \mathbf{x}_3. \end{aligned} \tag{4.9.2}$$

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[1] Drake, Peirce and Dow: Phys. Rev., **35**, 613 (1930).

[2] The proof is simple. By construction,

$$\mathbf{p} = (\mathbf{p}, \mathbf{l}_2)\, \mathbf{l}_2 + (\mathbf{p}, \mathbf{l}_3) \mathbf{l}_2$$

so that

$$\begin{aligned}\mathbf{M}^{-1}\, \mathbf{p} / X = \mathbf{r} &= (\mathbf{r}\, \mathbf{M}\, \mathbf{l}_2)\, \mathbf{M}^{-1}\, \mathbf{l}_2 + (\mathbf{r}\, \mathbf{M}\, \mathbf{l}_3)\, \mathbf{M}^{-1}\, \mathbf{l}_2 \\ &= (\mathbf{r}, \mathbf{x}^*_2)\, \mathbf{x}_2 + (\mathbf{r}, \mathbf{x}^*_3)\, \mathbf{x}_3 \end{aligned}$$

and since $(\mathbf{x}^*_1, \mathbf{x}_2) = (\mathbf{x}^*_1, \mathbf{x}_3) = 0$ by (4.7.8), $\mathbf{r}$ has components only in the plane of $\mathbf{x}_2$ and $\mathbf{x}_3$.

A straight line $y = a + bz$ will in general intersect the curve $y = 1 - z^{1/2}$ at 2 points; suppose we write $1 - z^{1/2} = a + bz$ and determine a and b so that the points of intersection will be ζ_2 and ζ_3; that is, we solve

$$1 - \sqrt{\zeta_2} = a + b\,\zeta_2$$

$$1 - \sqrt{\zeta_3} = a + b\,\zeta_3$$

for a and b and obtain

$$a = 1 - \frac{\sqrt{\zeta_2\zeta_3}}{\sqrt{\zeta_2} + \sqrt{\zeta_3}},\; b = -\frac{1}{\sqrt{\zeta_2} + \sqrt{\zeta_3}}\,. \tag{4.9.3}$$

Then using again the properties of eigenvectors and the fact that $\mathbf{r}$ is perpendicular to $\mathbf{x}^*_1$, we may write (as may be verified by substituting (4.9.3) and comparing with (4.9.2))

$$(1 - \mathbf{H}^{1/2})\,\mathbf{r} = (a + b\mathbf{H})\,\mathbf{r}, \tag{4.9.4}$$

and use this formula with the above values of a and b for numerical computation.

We obtain the characteristic values ζ_j by solving the cubic equation

$$|h_{ji} - \delta_{ji}\,\zeta| = (\zeta - \zeta_1)\,(\zeta - \zeta_2)\,(\zeta - \zeta_3) = 0.$$

Knowing $\zeta_1 = 1$, we only require the sum and the product of the two roots ζ_2 and ζ_3. We write the cubic in the form

$$\zeta^3 - I_1\,\zeta^2 + I_2\,\zeta - I_3 = 0$$

and identify two invariants of the matrix H

$$I_1 = \zeta_1 + \zeta_2 + \zeta_3 = h_{11} + h_{22} + h_{33} \tag{4.9.5}$$

and

$$I_2 = \zeta_1\,\zeta_2 + \zeta_2\,\zeta_3 + \zeta_3\,\zeta_1 =$$

$$= h_{11}\,h_{22} + h_{22}\,h_{33} + h_{33}\,h_{11} - h_{12}\,h_{21} - h_{23}\,h_{32} - h_{31}\,h_{13}. \tag{4.9.6}$$

Since $\zeta_1 = 1$,

$$\zeta_2 + \zeta_3 = I_1 - 1 \quad\text{and}\quad \zeta_2\,\zeta_3 = I_2 - I_1 + 1.$$

We have to calculate

$$\sqrt{\zeta_2\,\zeta_3} = (I_2 - I_1 + 1)^{1/2},\; \zeta_2 + \zeta_3 = I_1 - 1,$$

and

$$\sqrt{\zeta_2} + \sqrt{\zeta_3} = \sqrt{(\zeta_2 + \zeta_3) + 2\sqrt{\zeta_2\,\zeta_3}}$$

from the elements of the matrix H by using (4.9.5) and (4.9.6). This gives the following values for the constants of (4.9.4)

$$a = 1 - \frac{\sqrt{I_2 - I_1 + 1}}{\sqrt{I_1 - 1 + 2\sqrt{I_2 - I_1 + 1}}} \tag{4.9.7}$$

$$b = \frac{-1}{\sqrt{I_1 - 1 + 2\sqrt{I_2 - I_1 + 1}}}\,. \tag{4.9.8}$$

For three ions of valence ± 1, one of the ionic ratios, say μ_3 is $1/2$, so that $\mu_2 = \frac{1}{2} - \mu_1$, and we may express all the elements of H in terms of μ_1. If we define

$$\omega_{ji} = \frac{\omega_j}{\omega_i + \omega_j} \quad \text{where } \omega_{ij} + \omega_{ji} = 1,\ \omega_{jj} = 1/2,$$

then

$$h_{ji} = \mu_\sigma \omega_{\sigma j} \delta_{ji} + \mu_i \omega_{ij}. \tag{4.9.9}$$

4.10. *Examples of Computation.*

We shall now illustrate this method by computing the conductance at 18° for a solution containing 0.02 mols HCl and 0.08 mols KCl per liter. Then, using Kohlrausch's values of $\Lambda^\circ{}_j$, we have the following data:

Ion	j	$m_j = \Gamma_j$	μ_j	$\Lambda^\circ{}_j$	
H^+	1	0.02	0.1	315	$\omega_{12} = 0.8298$
K^+	2	0.08	0.4	64.6	$\omega_{13} = 0.8279$
Cl'	3	0.10	0.5	65.5	$\omega_{23} = 0.4965$

The matrix H is

$$\begin{pmatrix} 0.2541 & 0.0681 & 0.0860 \\ 0.0830 & 0.7348 & 0.2518 \\ 0.0828 & 0.1986 & 0.7814 \end{pmatrix}$$

and the invariants are

$$I_1 = 1.6712 + 0.9910\,\mu_1 = 1.7703$$

$$I_2 = 0.7567 + 1.3772\,\mu_1 + 0.2186\,\mu_1^2 = 0.8966.$$

Then, using (4.9.4), (4.9.7) and (4.9.8)

$$(1 - H^{1/2}) = 0.7080 - 0.8217\,H.$$

Since we are dealing with symmetrical electrolytes, the second term of the vector $\mathfrak{r}$ in (4.7.11) vanishes, and $\mathfrak{r}$ has the components $r_1 = 1, r_2 = 1, r_3 = -1$. The product (4.9.4) is now readily evaluated:

$$(1 - H^{1/2})_{1\sigma} r_\sigma = 0.7080\, r_1 - 0.8217\, H_{1\sigma} r_\sigma$$

$$= 0.7080 - 0.8217\,(0.2541 + 0.0681 - 0.0860) = 0.5139$$

$$(1 - H^{1/2})_{2\sigma} r_\sigma = 0.2429 \text{ and } (1 - H^{1/2})_{3\sigma} r_\sigma = -0.2971.$$

By (4.7.13) and (4.6.7), with $\Gamma = 0.2$,

$$-\frac{\Delta X_j}{X} = 0.5416\,\Gamma^{1/2} z'_j (1 - H^{1/2})_{j\sigma} r_\sigma = 0.2423\, z'_j (1 - H^{1/2})_{j\sigma} r_\sigma. \tag{4.10.1}$$

Now $\Delta X_j/X$ measures the relaxation correction to the conductance. Since the electrophoretic correction is independent of μ_1, we shall find it most interesting to confine our attention to the first correction. For either pure HCl or KCl at a concentration $\Gamma = 0.2$,

$$-\Delta X_j/X = 0.159\,\Gamma^{1/2} = 0.0711$$

for each ion.[1]

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[1] Onsager: II, equation (65).

We have tabulated in the first column below $\Delta X_j/X$ calculated by means of (4.10.1) for the mixture of HCl and KCl under consideration; the second column $\Delta\Lambda_j/\Lambda^\circ_j$ gives the difference between these figures and 0.0711, reckoned as percent change of conductance, and the third column the corresponding changes $\Delta\Lambda_j$ in conductance.

TABLE I

j	$\Delta X_j/X$	$100\,\Delta\Lambda_j/\Lambda^\circ_j$	$\Delta\Lambda_j$
1	0.1245	-5.34	-16.8
2	0.0589	$+1.22$	$+0.79$
3	0.0720	-0.09	-0.07

Assuming that our limiting laws (4.8.1) were valid at a concentration $\Gamma = 0.2$, the conductance of hydrogen ion in the 4 to 1 mixture would be 16.8 units *less* than in 0.1 normal HCl ($\Gamma = 0.2$), that of the potassium ion would be increased by 0.8 units over its value in 0.1 normal KCl and that of the chloride ion decreased by about 0.1 unit. Actually, this concentration is in general too high for applying the limiting formulas of the electrostatic theory, but we may assume that the *difference* in conductance in a mixture and in a solution containing a single solute at the same ionic strength would be given by (4.8.1) to the right order of magnitude at least, and that the calculated difference for a given ion would agree more closely with experiment, the lower the total concentration of ions. We shall see in the following section that these predictions are verified.

For $s = 4$, the equation $|h_{ji} - \delta_{ji}\zeta| = 0$ which determines the characteristic numbers is of the fourth degree, and although one of these numbers ($\zeta_1 = 1$) is known, it is not convenient in general to compute the others. Expansion of the function $(1-H^{1/2})$ in a series will prove to be the most satisfactory method. We shall illustrate this method by computing the conductance changes at 18° in a solution containing 0.04995 mols HCl and 0.0502 mols KCl per liter; the method for $s = 4$ is entirely analogous. Our data are then as follows:

Ion	j	$m_j = \Gamma_j$	μ_j	Λ°_j
H^+	1	0.04995	0.2495	315
K^+	2	0.05016	0.2505	64.6
Cl'	3	0.1001	0.5000	65.5

The matrices are

$$(h_{ji}) = \begin{pmatrix} 0.3782 & 0.0426 & 0.0860 \\ 0.2070 & 0.7094 & 0.2518 \\ 0.2066 & 0.1244 & 0.8310 \end{pmatrix}$$

$$(2h_{ji} - \delta_{ji}) = \begin{pmatrix} -0.2436 & 0.0853 & 0.1721 \\ 0.4140 & 0.4188 & 0.5036 \\ 0.4132 & 0.2488 & 0.6620 \end{pmatrix}$$

By means of the recursion formula (4.7.12) we now compute the vectors $\mathbf{r}^{(n)}$, for example

$$r^{(1)}{}_1 = (2H - 1)_{1\sigma}r_\sigma = (-0.2346 + 0.0853 - 0.1721) = -0.3304.$$

The following table gives the first four:

TABLE II

n	$r^{(n)}_1$	$r^{(n)}_2$	$r^{(n)}_3$
0	+1	+1	−1
1	−0.3304	0.3292	0.0000
2	0.1086	0.0011	−0.0546
3	−0.0358	0.0180	0.0091
4	0.0118	−0.0027	−0.0043

The sums $\sum_{n=0}^{\infty} c_n r^{(n)}_j$ may now be evaluated, using the values of the coefficients c_n given in (4.6.8); the first five terms of the series already give four place accuracy. The results of the calculations are given below, where the symbols are the same as those used in Table I.

TABLE III

Ion	j	$z'_j \Sigma c_n r^{(n)}_j$	$\Delta X_j/X$	$100\Delta\Lambda_j/\Lambda^\circ_j$	$\Delta\Lambda_j$
H^+	1	0.4212	0.1020	−3.09	−9.72
K^+	2	0.1758	0.0426	+2.85	+1.84
Cl'	3	0.2982	0.0723	−0.12	−0.08

The change of hydrogen ion conductance $\Delta\Lambda_1$ for an infinitesimal amount of HCl in 0.1 normal KCl is readily obtained by setting μ_1 zero: the following figures are self-explanatory:

$$(h_{ji}) = \begin{pmatrix} 0.1712 & 0.0851 & 0.0861 \\ 0 & 0.7518 & 0.2518 \\ 0 & 0.2483 & 0.7483 \end{pmatrix}$$

$$I_1 = 1.6712; \qquad I_2 = 0.7567$$

$$(1 - H^{1/2}) = 0.7391 - 0.8922\,H = a + bH$$

TABLE IV

j	r_j	$H_{j\sigma} r_\sigma$	$z'_j(a+bH)_{j\sigma} r_\sigma$	$\Delta X_j/X$	$100\Delta\Lambda_j/\Lambda^\circ_j$	$\Delta\Lambda_j$
1	1	0.1702	0.5872	0.1423	7.13	22.4
2	1	0.5000	0.2930	0.0710	0	0
3	−1	0.5000	0.2930	0.0710	0	0

Our result is that the limiting equivalent conductance of hydrogen ion in 0.1 KCl would be 22.4 units less than the conductance of hydrogen ion in 0.1 HCl. This is the result calculated by Bennewitz, Wagner and Küchler who have given a solution of the general equation (4.4.2) for the case $s = 3$, valid when one of the ions is present in infinitesimal amount.

4.11. *Comparison with Experiment.*

The change of conductance due to the "mixture effect" has been computed for several sets of published data. Bennewitz, Wagner and Küchler[1] have de-

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[1] Bennewitz, Wagner and Küchler: Loc. cit.

termined the transference numbers of Ba^{++}, H^+, K^+ and Cl' in various mixtures of $BaCl_2$ and HCl and of KCl and HCl at 18°. The concentrations used in our two examples in the description of the method of computation were taken from their data. Table V compares their observed results with our computed values:

TABLE V

	0.05 KCl – 0.05 HCl calc.	obs.	0.08 KCl – 0.02 HCl calc.	obs.
$\Delta\Lambda_1(H^+)$	−9.72	−10	−16.8	−12.8
$\Delta\Lambda_2(K^+)$	+1.84	+0.9	+ 0.8	—

Longsworth[1] has measured the migration velocities of individual ions in mixtures of HCl and KCl at 25° in which the chloride ion concentration was kept constant at 0.1 normal ($\Gamma = 0.2$). Table VI compares his results with those calculated[2] by means of (4.8.2).

TABLE VI

μ_1	$\Delta\Lambda_1(H^+)$ calc.	obs.	$\Delta\Lambda_2(K^+)$ calc.	obs.	$\Delta\Lambda_3(Cl')$ calc.	Λ_3 obs.
0.500[a]	0.00	—	+3.86	(2.36)	0.000	66.32
0.375	− 5.14	−2.56	3.00	2.06	0.063	66.19
0.250	−10.81	−5.06	2.09	0.96	0.097	66.07
0.125	−17.24	−8.06	1.10	0.56	0.086	65.83
0.000[b]	−24.79	(−10.96)	0.00	—	0.000	65.75

[a] pure HCl [b] pure KCl.

The "observed" values in parentheses were obtained by Longsworth by linear extrapolation of his data. Fig. 4 summarizes the calculated and observed results for H^+ and Fig. 5 for K^+. Bennewitz' data are indicated by crosses, Longsworth's by circles and the theoretical curve is drawn solid. The theoretical curve depends on the mixing ratio in a rather complicated way; both graphs exhibit a slight curvature. Longsworth's results lie on a smooth curve which is approximately of the same form as the theoretical, although due to the high concentration, the numerical values differ by about a factor of two. Bennewitz, Wagner and Küchler obtained their results by the Hittorf method, while Longsworth employed the method of moving boundaries. The latter method is probably capable of greater accuracy, and in fact, the effects measured by Longsworth fall beneath the calculated values by amounts that might reasonably correspond to the mathematical approximations allowed in the theory.

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[1] Longsworth: J. Am. Chem. Soc., 52, 1897-1910 (1930).

[2] We used the following values in order to compute the results for the 25° experiments: $\Lambda_\infty(HCl) = 426.0$, $\Lambda_\infty(NaCl) = 126.42$, $\Lambda_\infty(KCl) = 149.84$; t_K (KCl) = 0.4905. t_K = limiting transference number of K^+ in KCl. We are indebted to Dr. MacInnes, Dr. Longsworth and Dr. Shedlovsky for permission to use these figures in advance of their publication.

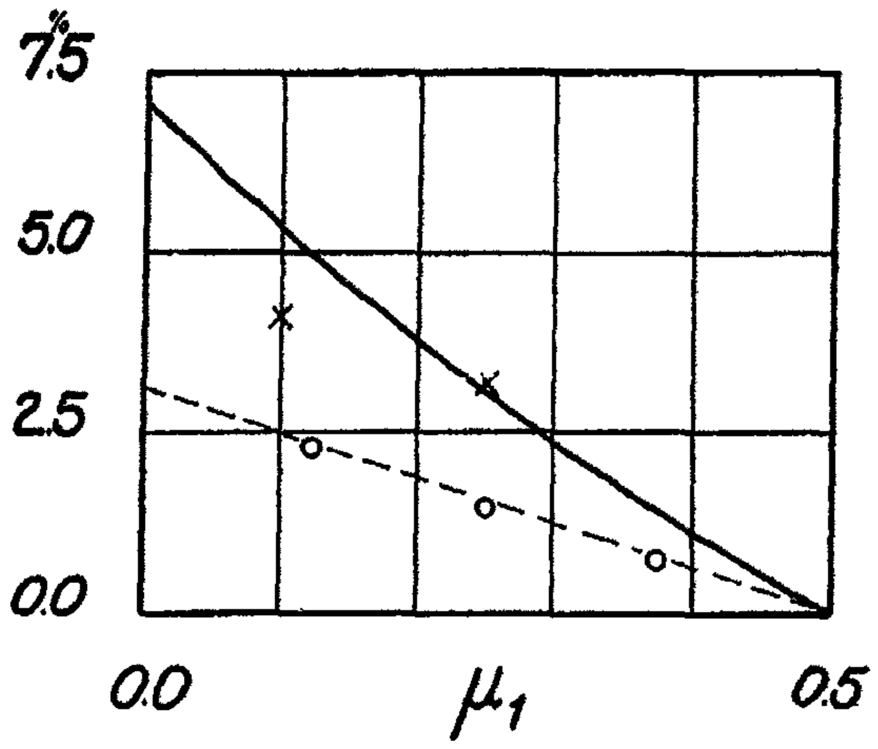

FIG. 4
Variation of Hydrogen Ion Conductance in HCl-KCl Mixtures

Fig. 6 shows the calculated mixture effect for the common ion (Cl' in HCl and KCl); the effect is so small that it was necessary to magnify the scale (50 times compared to figures 4 and 5). The maximum effect is apparently within the experimental error, and as seen from Table VI, is masked by a specific difference in Λ_{Cl} between HCl and KCl; we have therefore tabulated Λ_3 instead of $\Delta\Lambda_3$.

As a final example, we have chosen the data of Bray and Hunt[1] on the specific conductance of mixtures of NaCl and HCl at 25°. If there were no mixture effect, one could compute the specific conductance κ of a solution containing m_1 mols NaCl and m_2 mols HCl from the conductance Λ_{NaCl} of NaCl in m_1 normal solution and that of HCl, Λ_{HCl}, in m_2 HCl by the formula

$$1000\kappa = m_1\Lambda_{NaCl} + m_2\Lambda_{HCl}.$$

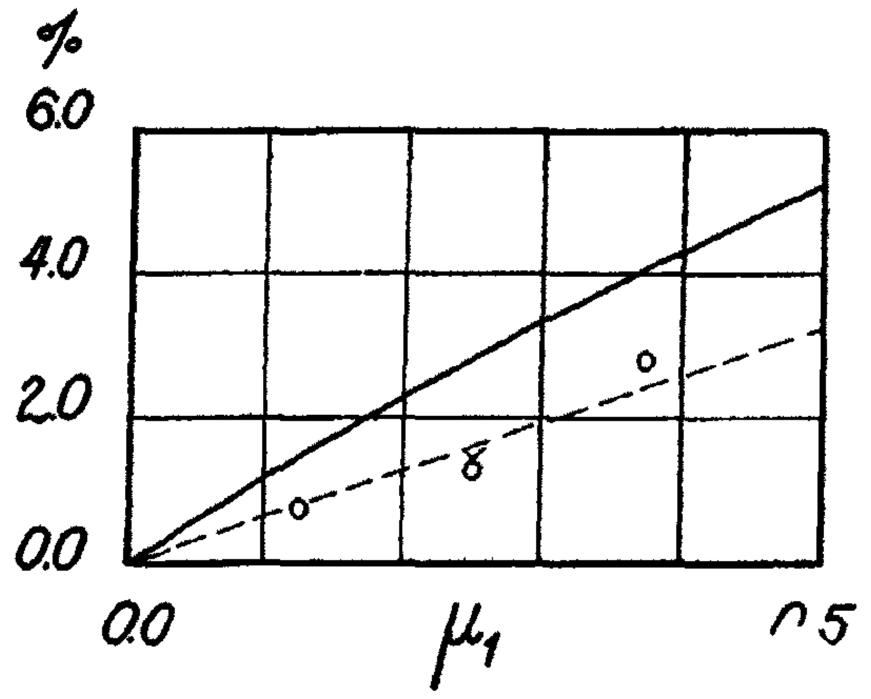

FIG. 5
Variation of Potassium Ion Conductance in HCl-KCl Mixtures

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[1] Bray and Hunt: J. Am. Chem. Soc., **33**, 781 (1911).

These values have been computed from Bray and Hunt's data on pure NaCl and pure HCl solutions. Then the observed specific conductances were subtracted from the additive conductances, to give "$\Delta\kappa$ observed", the deviations from additivity due to the mixture effect. By means of (4.8.2), we calculated the change of conductance due to the presence of 3 kinds of ions as before, and then computed the sum $m_1\Delta\Lambda_1 + m_2\Delta\Lambda_2 + m_3\Delta\Lambda_3$ as "$\Delta\kappa$ calculated." The results are given in Table VII: (concentrations in millimols).

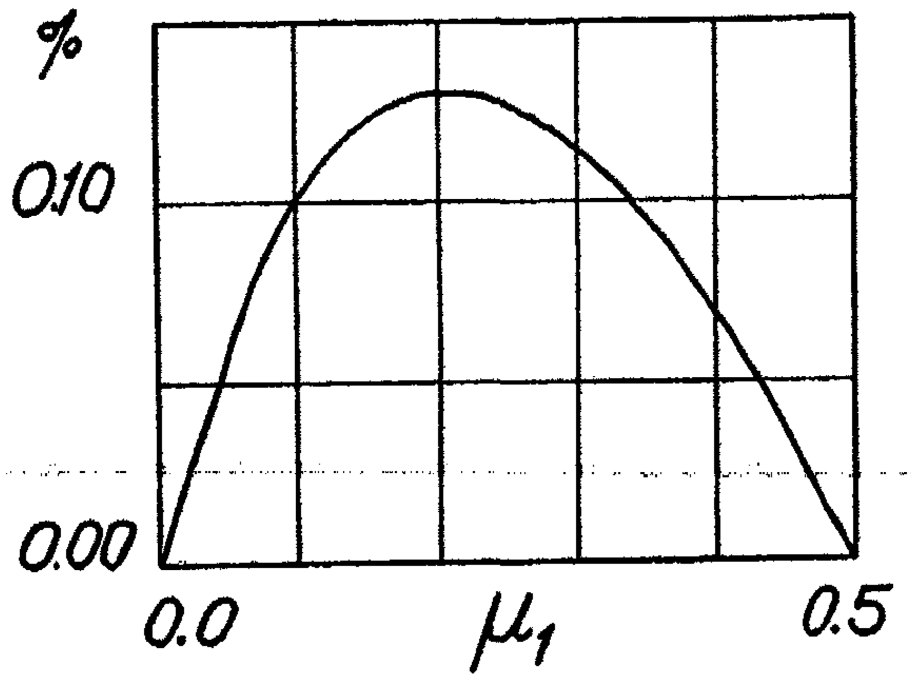

FIG. 6

Variation of Chloride Ion Conductance in HCl-KCl Mixtures

TABLE VII

Conc. HCl	Conc. NaCl	$\Delta\kappa \times 10^3$ obs.	$\Delta\kappa \times 10^3$ calc.	% obs.	% calc.
100	100	0.94	1.56	1.99	3.31
50*	100	0.50	0.95	1.72	3.29
20*	100	0.26	0.45	1.44	2.50
10	100	0.15	0.24	1.05	1.68
5	100	0.08	0.12	0.64	0.98
2	100	0.04	0.05	0.35	0.42
50	20	0.17	0.248	0.78	1.14
20	20	0.103	0.139	1.02	1.38
10	20	0.061	0.085	0.98	1.35
4	20	0.034	0.040	0.88	1.03
2	20	0.021	0.021	0.68	0.71
1	20	0.011	0.011	0.40	0.41
12.5	5	0.028	0.0311	0.50	0.55
5	5	0.020	0.0174	0.76	0.66
2.5	5	0.010	0.0106	0.62	0.65
1	5	0.005	0.0050	0.49	0.49

The two experiments marked with an asterisk are in about the same range of concentration and mixing ratio as the KCl-HCl mixtures discussed above, and again the calculated result is about twice the observed. It will be noted, however, that the calculated figures agree more closely with experiment, the smaller μ_1 and Γ become. Also, the calculated values for $\Delta\kappa$ duplicate the observed flat maximum of $\Delta\kappa$ at the equal mixture of NaCl and HCl.

The experiments of Bray and Hunt indicate that if the individual mobilities in a mixture were measured at low concentrations, not only the type, but also the absolute magnitude of the mixture effect would be found to agree with the theory.

4.12. *The General Equations for Diffusion.*

Fick's law for diffusion in a two-component system is ordinarily written

$$c\,\mathbf{v} = \mathbf{J} = -D \operatorname{grad} c, \tag{4.12.1}$$

where D is the coefficient of diffusion, $\mathbf{v}$ the velocity, $\mathbf{J}$ the flow and c the concentration (amount per unit volume) of solute. The flow is usually defined relative to a fixed plane in the solution, which is assumed "at rest." This convention has the esthetic advantage that no distinction is made between solute and solvent, both obeying (4.12.1) with the same coefficient of diffusion D. Moreover, the ideal case of "self-diffusion" (interdiffusion of isotopes) is most simply described in this form; D becomes independent of the mixing ratio. In a general case, however, it is somewhat awkward to define a solution "at rest" during diffusion, particularly when the mixing of the substances involved causes an appreciable change of volume. We must bear in mind that the concentration gradient determines only the local *relative* flow of solute and solvent, and that a bulk motion of the solution, dependent on other conditions, may be superimposed.

In the following, we shall assume that one (solvent) constituent of the solution is present in dominating quantity. The flow of any solute constituent will be defined *relative to a local frame of reference moving with the solvent.* This simpler convention seems definitely preferable in the case of electrolytes, which are in any case hardly amenable to a symmetrical consideration of solute and solvent. If a symmetrical formulation is desired, one may define a "bulk velocity"

$$\bar{\mathbf{v}} = \Sigma\, \mathbf{J}_i \overline{V}_i = \Sigma\, c_i \mathbf{v}_i \overline{V}_i, \tag{4.12.2}$$

where $(\overline{V}_0), \overline{V}_1, \ldots, \overline{V}_s$ are the partial volumes of the constituents (0), 1, . . . , s; apparently there is no reasonable alternative to this choice. We may assume that either the velocity of the solvent or the "bulk velocity" (4.12.2) obeys the hydrodynamic laws; the difference is of no practical importance.

Fick's law (4.12.1) may be written in the alternative form

$$\mathbf{J} = -\Omega \operatorname{grad} \mu, \tag{4.12.3}$$

where μ is the chemical potential, and the coefficient of diffusion equals

$$D = \Omega(\partial\mu/\partial c)_{p,T}. \tag{4.12.4}$$

In the special case of an ideal solution

$$\partial\mu/\partial c = RT/c,$$

so that

$$RT\,\Omega = cD.$$

In general, (4.12.4) may be rewritten in terms of activity coefficients f:

$$cD = RT\Omega\,(1 + c\,\partial \log f/\partial c). \qquad (4.12.5)$$

In the case of electrolytes, the correction term involving f is negative, except in some cases at relatively high concentrations (cf. § 4.13). It has been suggested that the variation of D with concentration might be accounted for entirely by this deviation from ideal thermodynamic behavior, and that Ω/c = const. As we shall see in the following, the theory predicts that Ω/c will also vary with the concentration, although much less than D. According to (4.12.3), the ratio Ω/c equals the "mobility," that is the velocity caused by a unit force $\mathbf{k} = -\text{grad}\ \mu$, (cf. § 4.1).

The natural generalization of (4.12.3) to the case of several solute substances is

$$\mathbf{J}_i = -\sum_{k=1}^{s} \Omega_{ik}\ \text{grad}\ \mu_k,\ (i = 1, \ldots, s), \qquad (4.12.6)$$

assuming a *linear* relation between velocities and potential gradients for the solute substances 1, 2, . . ., s. The matrix of coefficients (Ω_{ik}) is symmetrical

$$\Omega_{ik} = \Omega_{ki}. \qquad (4.12.7)$$

This reciprocal relation states that the flow of constituent no. 7 caused by a unit force per unit amount of no. 3 will equal the flow of no. 3 caused by a unit force on substance no. 7. Relations of this type are included in the "principle of the least dissipation of energy," which has been derived[1] from the assumption of microscopic reversibility. We shall show at the end of this section, assuming the principle of the least dissipation, that the symmetry relation (4.12.7) applies independently of the frame of reference for the flow, which is not quite obvious.

By solving the system of equations (4.12.6) for grad μ_1, . . ., grad μ_s, we obtain an alternative formulation of some interest, namely

$$-\text{grad}\ \mu_i = \sum_{k=i}^{s} R_{ik}\,\mathbf{J}_k,\ (i = 1, \ldots s), \qquad (4.12.8)$$

where the coefficients (R_{ik}) form the reciprocal matrix of (Ω_{ik}), and on account of the symmetry of the latter,

$$R_{ik} = R_{ki}. \qquad (4.12.9)$$

Thanks to this symmetry, we only need to know the *dissipation-function*

$$2\,F(\mathbf{J},\mathbf{J}) = \sum_{i,k=1}^{s} R_{ik}\,(\mathbf{J}_i,\mathbf{J}_k) = \sum_{i,k} n_i n_k R_{ik}((\mathbf{v}_i-\mathbf{v}_o),(\mathbf{v}_k-\mathbf{v}_o)), \qquad (4.12.10)$$

and (4.12.8) may be written

$$\text{grad}\ \mu_i + \partial F/\partial \mathbf{J}_i = 0,\ (i = 1, \ldots, s), \qquad (4.12.11)$$

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[1] L. Onsager: Phys. Rev., 37, 405 (1931).

or in a variation-principle for convenient transformation

$$\delta(T\dot{S} - F) = 0, \tag{4.12.12}$$

where $\dot{S}$ is the rate of production of entropy; according to thermodynamics

$$T\, dS/dt = T\dot{S} \equiv -\Sigma\, (\mathbf{J}_i \cdot \text{grad}\ \mu_i). \tag{4.12.13}$$

The formulation (4.12.12) satisfies all esthetic requirements.

In the case of an ideal solution containing solute molecules of the species 1, . . . s, the solute molecules might be expected to diffuse *independently* according to the law

$$\mathbf{J}_i = -\Omega_{ii}\ \text{grad}\ \mu_i,\ (i = 1, \ldots, s); \tag{4.12.14}$$

it also seems probable that the mobilities Ω_{ii}/c_i would not vary more with the composition than the fluidity of the solution. In the case of a solution that exhibits deviations from the ideal laws due to compound formation between the solute substances, we should expect that one migrating substance could carry another along, and that the coefficients Ω_{ik}, $(i \neq k)$, would not all vanish. On this picture, if the simple law (4.12.14) is valid for the different species of molecules and molecular compounds actually present, the reciprocal relation (4.12.14) evidently holds. In many instances, however, attempts to describe all deviations from ideal laws in terms of molecular compounds lead to awkward difficulties, and the interpretation is usually ambiguous. Therefore, where a noncommittal phenomenological description will not suffice, it is preferable, when possible, to construct a more detailed physical picture, and to allow explicitly for the forces between the molecules. This applies particularly to electrolytes.

In dealing with electrolytes, it is convenient to describe conduction and diffusion by one combined scheme, so that (4.12.6) now relates the rates of flow $\mathbf{J}_1, \ldots, \mathbf{J}_s$ of *ionic* species 1, . . ., s to the gradients of the *total potentials*

$$\mu_i = \mu_i' + e_i\varphi, \tag{4.12.15}$$

of the ions, where φ is the electrostatic potential, (cf. § 4.1). The generalization to the case where the electric field does not possess a potential is obvious. In the limit of low concentrations, the ions migrate independently (ideal case)

$$\Omega_{ik} = 0,\ (i \neq k);$$
$$\Omega_{ii} = n_i\omega_i,$$

where ω_i is the "mobility" of a single ion (in this notation, the electrolytic electrolytic mobility is $e_i\omega_i$ where e_i is the charge). At higher concentrations as shown by our calculations in §§ 4.1-7, the ions will interfere with each others' motion; the order of magnitude of this effect is given by

$$\Omega_{ik} = O(n_i n_k\, 4\pi\omega d_0^2/\kappa) \pm O(n_i n_k d_0/\kappa\eta),$$

with $d_0 = |e_i e_k|/DkT$ and otherwise the notations of §§ (1.3) and (4.1); the first term is due to direct transfer of forces, the second to electrophoresis. There are similar corrections to Ω_{ii}:

$$\Omega_{ii} = n_i\omega_i - O(n_i\omega_i\kappa d_0) - O(n_i^2 d_0/\kappa\eta).$$

Since $\kappa \sim n^{1/2}$, the relative effects of interaction are proportional to the square root of the concentration, in the sense that doubling all concentrations increases the effects by a factor $\sqrt{2}$.

The symmetry condition (4.12.7) for (Ω_{ik}) holds for the migration of ions as well, if we allow the assumption of microscopic reversibility. While this assumption is nowhere explicitly introduced into our calculations, we shall see that the results conform to the reciprocal relation (4.12.7). The reason is, of course, that the assumed mechanism of interaction between the ions is in accord with the general principle. Indeed: The forces between the ions possess a potential, and so does the Brownian motion, because the relation of neighborhood is a reciprocal one; the hydrodynamic interaction of ions also obeys the same reciprocal relations because the principle of the least dissipation of energy[1] is valid for (slow) motion of viscous fluids.

The equations for migration of ions may be given the form (4.12.8) or (4.12.11-12); in the case of ions, $\mu_1, \ldots, \mu_s$ in (4.12.13) stand for the total potentials (4.12.15). The results of our calculations will be summarized in a very compact form by the construction of a dissipation-function.

We have promised to derive the reciprocal relation (4.12.7) from the principle of the least dissipation. We shall prefer to obtain its equivalent (4.12.9). Let us consider a case of parallel flow in unit cross-section, so that the volume element $dV = dx$. The flow $\mathbf{J}_i$ is defined relative to a frame of reference (ξ, y, z) which may move with the velocity of the solvent, or with the "bulk velocity" (4.12.2); in the latter case we could assume $\xi = x$. In any case there exists a *dissipation-function*

$$2F \equiv 2T\Phi \equiv \int \Sigma R_{ik}\mathbf{J}_i\mathbf{J}_k\, dx.$$

In order to apply the general principle (4.12.12)

$$\delta(\dot{S} - \Phi) = 0,$$

we must express $\dot{S}$ in the variables $\mathbf{J}_i$. For this purpose, write

$$n_k dx/d\xi = N_k,$$

then $N_k d\xi$ is the amount of k ions contained in the deformable volume element $d\xi$. According to thermodynamics

$$T(\dot{S} + \dot{S}^*) = -\int_{x'}^{x''} \Sigma \mu_k \frac{dN_k}{dt}\, d\xi - \Sigma\, [\mu_k \mathbf{J}_k]_{x'}^{x''},$$

where $\dot{S}^*$, corresponding to the term in brackets, denotes the external entropy change (omitted above for simplicity). Now the equation of continuity

$$\frac{\partial \mathbf{J}_k}{\partial \xi} = -\frac{\partial N_k}{\partial t}$$

is valid in deformable coordinates as well, hence

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[1] This principle may be stated: When a force of magnitude X, applied at a point A in the direction (1), will cause a velocity $\mathbf{v}$ in the direction (2) at the point B, then conversely, the force X applied at B in the direction (2) will cause a velocity $\mathbf{v}$ in the direction (1) at A.

$$T\dot{S} = \int_{x'}^{x''} \Sigma\, \mu_k \frac{d\mathbf{J}_k}{d\xi}\, d\xi = \int_{x'}^{x''} \Sigma\, \mu_k d\mathbf{J}_k =$$

$$= \Sigma\, [\mu_k \mathbf{J}_k]_{x'}^{x''} - \int_{x'}^{x''} \Sigma\, \mathbf{J}_k\, d\mu_k$$

and

$$T(\dot{S} + \dot{S}^*) = -\int_{x'}^{x''} \Sigma\, \mathbf{J}_k\, d\mu_k = -\int_{x'}^{x''} \Sigma\, \mathbf{J}_k\, d\mu_k\, dx.$$

Now the principle of the least dissipation yields

$$0 = T\,\delta(\dot{S} + \dot{S}^* - \Phi) =$$

$$= \int_{x'}^{x''} \sum_i \left(-\frac{\partial \mu_i}{\partial x} - \frac{1}{2} \frac{\partial}{\partial \mathbf{J}_i} (\sum_{k,j} R_{kj} \mathbf{J}_k \mathbf{J}_j) \right) \delta \mathbf{J}_i\, dx = 0,$$

whence

$$-\frac{\partial \mu_i}{\partial x} = \sum_k R_{ik} \mathbf{J}_k,$$

where

$$R_{ik} = R_{ki},$$

because the linear form is obtained by differentiation of a quadratic.

4.12. *Diffusion of a Simple Electrolyte.*

In an electrolyte containing only two kinds of ions, the condition for no electric current is that anions and cations migrate with the same velocity

$$\mathbf{v}_1 = \mathbf{v}_2 = \mathbf{v}; \quad \mathbf{J}_1 = n_1 \mathbf{v}; \quad \mathbf{J}_2 = n_2 \mathbf{v}. \tag{4.13.1}$$

In the limit of low concentrations, the interaction between ions (except the space charge that prevents an electric current) may be neglected, and we have

$$\mathbf{v} = \mathbf{k}_1 \omega_1 = \mathbf{k}_2 \omega_2 = -\omega_1 \operatorname{grad} \mu_1 = -\omega_2 \operatorname{grad} \mu_2. \tag{4.13.2}$$

In this "zero" approximation, the "forces" $\mathbf{k}_1$ and $\mathbf{k}_2$ on the individual ions are given by (4.13.2) and

$$\mathbf{k} = \nu_1 \mathbf{k}_1 + \nu_2 \mathbf{k}_2 = -\operatorname{grad} \mu,$$

where μ is the chemical potential of a molecule dissociating into ν_1 anions and ν_2 cations. We obtain

$$\mathbf{k}_1 = \frac{-\rho_1}{\nu_1 \rho_1 + \nu_2 \rho_2} \operatorname{grad} \mu = \frac{-\omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \operatorname{grad} \mu;$$

$$\mathbf{k}_2 = (\rho_2/\rho_1)\mathbf{k}_1 = (\omega_1/\omega_2)\mathbf{k}_2, \tag{4.13.3}$$

and

$$\mathbf{v} = \frac{-\omega_1 \omega_2}{\nu_1 \omega_1 + \nu_2 \omega_2} \operatorname{grad} \mu. \tag{4.13.4}$$

Here, if the solution is assumed ideal in regard to its thermodynamic properties, so that

$$\operatorname{grad} \mu = (\nu_1 + \nu_2)\, (kT/n) \operatorname{grad} n,$$

Nernst's formula[1]

$$\mathbf{J} = n\mathbf{v} = -\frac{(\nu_1 + \nu_2)}{\nu_1 \omega_1 + \nu_2 \omega_2}\, \omega_1 \omega_2\, kT \operatorname{grad} n \tag{4.13.5}$$

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[1] Nernst: Loc. cit.

results. When the forces between the ions are taken into account, the main effect consists in a contribution to the thermodynamic potential; we have now

$$\operatorname{grad}\mu = (\nu_1 + \nu_2)\, kT \operatorname{grad} \log (fn), \qquad (4.13.6)$$

where f is the mean activity coefficient of the ions, for low concentrations[1] given by the limiting law

$$\log f = e_1e_2\, \kappa/2DkT. \qquad (4.13.7)$$

We thus allow for the interionic attraction reducing the "thermodynamic" tendency of the ions to separate by diffusion; it remains to compute the effect of interaction on the *mobility* of the migrating ions.

We first note that the diffusion of a *simple* electrolyte will not be obstructed by the effect which Debye and Hückel named "ionic forces," the retardation of a migrating ion by an asymmetric field in its atmosphere. The reason is that all ions migrate with the same velocity, so that an atmosphere needs no coercion to follow its central ion; in consequence, the atmosphere is displaced as a whole, undisturbed, and develops no asymmetry. This can be verified already in our fundamental equations (4.3.2) by substituting

$$\mathbf{k}_1\omega_1 = \mathbf{k}_2\omega_2;$$

the perturbation terms in (4.3.2) then cancel each other. (In calculating the first approximation for the effect, we may compute the perturbation terms from the "zero" approximation (4.13.2).) Of course, our final formulas for the "ionic forces" also yield a vanishing effect for this case; we may refer to formula (4.14.12) below.

Otherwise with the electrophoresis, this effect depends on a *volume force* attacking in the ionic atmosphere. According to (4.2.2) and (4.2.6), if the potential at a distance r from a j ion is $\psi_j(r)$, then the force density at this distance is

$$\mathbf{F} = -(n_1e_1\mathbf{k}_1 + n_2e_2\mathbf{k}_2)\,(\psi_j/kT) + \tfrac{1}{2}(n_1e_1^2\mathbf{k}_1 + n_2e_2^2\mathbf{k}_2)\,(\psi_j/kT)^2 - \ldots; \qquad (4.13.8)$$

Substituting (4.13.2), the first term in (4.13.8) vanishes when and only when $\omega_1 = \omega_2$; the second term is always positive. In § 4.2, we calculated the effect of the volume force (4.13.8) on the motion of the ions (assuming $\mathbf{k}_j = \mathbf{v}\rho_j$) and found for the resulting additional velocity (4.2.12)

$$\Delta\mathbf{v}_j = \mathbf{v}\left(-\frac{2}{3\eta}(n_1e_1\rho_1 + n_2e_2\rho_2)\frac{e_j}{DkT\;\kappa(1 + \kappa a)} + \frac{1}{3\eta}(n_1e_1^2\rho_1 + n_2e_2^2\rho_2)\left(\frac{e_j}{DkT}\right)^2\varphi(\kappa a)\right), \qquad (4.13.9)$$

$$(j = 1, 2)$$

with

$$\varphi(\kappa a) = e^{2\kappa a}\operatorname{Ei}(2\kappa a)/(1 + \kappa a)^2. \qquad (4.13.10)$$

The ultimate result of this effect is of course to alter the forces $\mathbf{k}_1$ and $\mathbf{k}_2$ that are needed to make both ions migrate with the same velocity $\mathbf{v}$: because in

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[1] Debye and Hückel: Physik. Z., **24**, 185 (1923).

pure diffusion, any velocity difference $\mathbf{v}_1 - \mathbf{v}_2$ will be eliminated by a readjustment of the electric field (space charge). Since both ions migrate relative to a moving immediate environment, we have now

$$\mathbf{k}_j = \rho_j(\mathbf{v} - \Delta\mathbf{v}_j),\ (j = 1, 2). \qquad (4.13.11)$$

Strictly speaking, this corrected force should be substituted in (4.13.9) in order to calculate $\Delta\mathbf{v}_j$, but our calculations are not accurate enough to warrant this refinement. When we use (4.13.9), as stands, for calculating the correction to $\mathbf{k}$, we obtain (cf. (4.2.13-14))

$$\begin{aligned} - \operatorname{grad} \mu = \mathbf{k} &= \nu_1\rho_1(\mathbf{v} - \Delta\mathbf{v}_1) + \nu_2\rho_2(\mathbf{v} - \Delta\mathbf{v}_2) = \\ &= \mathbf{v}\left(\nu_1\rho_1 + \nu_2\rho_2 + (\rho_1 - \rho_2)^2 \frac{\nu_1\nu_2}{(\nu_1 + \nu_2)} \frac{\kappa}{6\pi\eta(1 + \kappa a)}\right. \\ &\qquad \left. - \left\{\frac{\nu_2\rho_1 + \nu_1\rho_2}{\nu_1 + \nu_2}\right\}^2 \frac{\kappa^4\varphi(\kappa a)}{48\,\pi^2\eta n}\right) \end{aligned} \qquad (4.13.12)$$

for the "force" per molecule of solute (present in concentration $n = n_1/\nu_1 = n_2/\nu_2$ molecules/cm^3). The third term in the brackets is the "first order" electrophoretic effect, proportional to $\sqrt{n}$ (for $\kappa a << 1$). The last term is of the order $n \log n$, (second order), and always negative. The physical interpretation of the effect is interesting. If the ions were arranged at random, then the assembly of ions, moving as a whole with the velocity $\mathbf{v}$ against the solvent, would meet the same resistance as if the ions were moving in separate batches of solvent; the last two terms in (4.13.12) are due to deviations from a random arrangement, which affect the combined resistance. The reason for the first order effect, proportional to $(\rho_1 - \rho_2)^2$, is that the anions in the neighborhood of a given anion are partly replaced by cations, and vice versa near cations. If anions and cations are subject to the same frictional force, that is when $\rho_1 = \rho_2$, the replacement does not matter. However, when one species of ions is more mobile than the other, then the sluggish ions will move in a countercurrent (consider the first term in (4.13.9)), while the mobile ions will be aided by a motion of their environment, whereby

$$n_1\Delta\mathbf{v}_1 + n_2\Delta\mathbf{v}_2 = 0.$$

The compensation of the corresponding forces is incomplete; hence the first order term in (4.13.12). The second-order (last) term depends simply on an overall reduction of the mean distances between the ions in the sense that the distances between ions of opposite sign are reduced more than the distances between ions of the same sign are increased. This effect always decreases the resistance to diffusion; we here meet for the first time a case where *the Coulomb forces between the ions aid a transport process.*

We obtain the equation for diffusion in the form (4.12.3) by solving (4.13.12) for $\mathbf{v}$ and multiplying by n. Within the limits of accuracy of our calculations we may neglect second and higher powers of the corrections $\Delta\mathbf{v}_1$ and $\Delta\mathbf{v}_2$ due to Coulomb forces between the ions, which gives

$$\mathbf{J} = n\mathbf{v} = -\Omega \operatorname{grad} \mu = -\left(\frac{n\omega_1\omega_2}{\nu_1\omega_2 + \nu_2\omega_1} + \Delta\Omega\right) \operatorname{grad} \mu, \qquad (4.13.13a)$$

where

$$\Delta\Omega = -\left(\frac{\omega_1 - \omega_2}{\nu_1\omega_2 + \nu_2\omega_1}\right)^2 \frac{\nu_1\nu_2}{\nu_1 + \nu_2} \frac{\kappa n}{6\pi\eta(1 + \kappa a)} +$$

$$\frac{(\nu_1\omega_1 + \nu_2\omega_2)^2}{(\nu_1 + \nu_2)^2 (\nu_1\omega_2 + \nu_2\omega_1)^2} \frac{\kappa^4\varphi(\kappa a)}{48\ \pi^2\ \eta}. \qquad (4.13.13b)$$

In converting this formula to macroscopic units, we must remember that

$$n = N\bar{n}; \quad N\mu = \bar{\mu},$$

where N is Avogadro's number, $\bar{n}$ the concentration in g.mols/cm^3, and $\bar{\mu}$ the chemical potential in ergs/g.mol.; hence

$$\bar{\mathbf{J}} = \bar{n}\mathbf{v} = -(\Omega/N^2) \operatorname{grad} \mu = \bar{\Omega} \operatorname{grad} \bar{\mu}.$$

Substituting (3.8.40), we find

$$\bar{\Omega} = \frac{10^{-7}\,\bar{n}}{F^2} \frac{\Lambda_1\Lambda_2}{\nu_1 z_1\ (\Lambda_1 + \Lambda_2)} + \Delta\bar{\Omega}' + \Delta\bar{\Omega}'', \qquad (4.13.15)$$

where $F = 96500$ coulomb and the first and second order correction terms are, respectively,

$$\Delta\bar{\Omega}' = -\left(\frac{z_2\Lambda_1 - z_1\Lambda_2}{\Lambda_1 + \Lambda_2}\right)^2 \frac{1}{z_1 z_2\ (\nu_1 + \nu_2)\,N} \frac{\kappa\bar{n}}{6\pi\eta(1 + \kappa a)}, \qquad (4.13.15a)$$

$$\Delta\bar{\Omega}'' = \left(\frac{z_2^2\Lambda_1 + z_1^2\Lambda_2}{\Lambda_1 + \Lambda_2}\right)^2 N^2\,\epsilon^4 \frac{(\bar{n})^2}{3\eta(DRT)^2}\,\varphi(\kappa a). \qquad (4.13.15b)$$

We are still retaining the abbreviation

$$\kappa = N\epsilon\sqrt{\frac{4\pi}{DRT} z_1 z_2\,(\nu_1 + \nu_2)\bar{n}}.$$

When we introduce the values given by Birge[1] for the universal constants and write $\Lambda_1 + \Lambda_2 = \Lambda$, $1000\,\bar{n} = m$ (g.mols/l.), we obtain

$$\bar{\Omega} = 1.074 \times 10^{-20} \frac{\Lambda_1\Lambda_2}{\nu_1 z_1\Lambda} m + \Delta\bar{\Omega}' + \Delta\bar{\Omega}'', \qquad (4.13.16a)$$

$$\Delta\bar{\Omega}' = -\frac{(z_2\Lambda_1 - z_1\Lambda_2)^2}{\Lambda^2\,z_1 z_2(\nu_1 + \nu_2)} \frac{3.111 \times 10^{-19}}{\eta\sqrt{DT}} \frac{m\sqrt{\Gamma},}{1 + \kappa a} \qquad (4.13.16b)$$

$$\Delta\Omega'' = \frac{(z_2^2\Lambda_1 + z_1^2\Lambda_2)^2}{\Lambda^2} \frac{9.18 \times 10^{-13}}{\eta(DT)^2}\,m^2\,\varphi(\kappa a), \qquad (4.13.16c)$$

$$\kappa = \frac{3.556 \times 10^9}{\sqrt{DT}} \sqrt{z_1 z_2(\nu_1 + \nu_2)m} = \frac{3.556 \times 10^4}{\sqrt{DT}} \sqrt{\Gamma}. \qquad (4.13.16d)$$

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[1] Birge: Phys. Rev. Supp., 1, 1 (1929).

Here the function $\varphi(\kappa a)$ is given by (4.13.10), and a is the mean diameter (least distance of approach) of anion and cation. For water as a solvent at 18°C we have $T = 291.2$; $D = 81.1$; $\eta = 0.01055$; hence

$$\Delta\bar{\Omega}' = -\frac{(z_2\Lambda_1 - z_1\Lambda_2)^2}{\Lambda^2} \times 19.2 \times 10^{-20} \frac{m^2}{\sqrt{\Gamma}\,(1 + A\sqrt{\Gamma})}, \quad (4.13.17)$$

$$\Delta\bar{\Omega}'' = \frac{(z_2^2\Lambda_1 + z_1^2\Lambda_2)^2}{\Lambda^2} \times 15.6 \times 10^{-20}\, m^2\varphi(A\sqrt{\Gamma}),$$

$$A = 0.232 \times 10^8\, a,\ \Gamma = z_1z_2(\nu_1 + \nu_2)\, m,$$

and for a univalent binary electrolyte

$$10^{20}\bar{\Omega}/m = 1.074\, \Lambda_1\Lambda_2/\Lambda - 9.60 \left(\frac{\Lambda_1 - \Lambda_2}{\Lambda_1 + \Lambda_2}\right)^2 \frac{\sqrt{2m}}{1 + A\sqrt{2m}} + 15.6m\,\varphi(A\sqrt{2m}). \quad (4.13.18)$$

The coefficient of diffusion (in c. g. s. units) is

$$D = \bar{\Omega}\, d\mu/d\bar{n} = 10^3\, \bar{\Omega}\, d\mu/dm.$$

For a binary electrolyte

$$m\, d\mu/dm = 2\, RT\, (1 + m\, d \log f/dm),$$

where f is the appropriate activity coefficient; hence at 18°C

$$D = 4.842 \times 10^{10}\, (\bar{\Omega}/m)\, (1 + m\, d \log f/dm). \quad (4.13.19)$$

A useful semi-empirical formula for f has been given by Hückel[1] namely

$$\log f = \frac{-0.820\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma, \quad (4.13.20)$$

where $A\sqrt{\Gamma} = \kappa a$, applicable to strong uni-univalent electrolytes in aqueous solution at 25°. Differentiating this formula we obtain

$$1 + m\, d \log f/dm = 1 - \frac{0.410\sqrt{2m}}{(1 + A\sqrt{2m})^2} + 2Bm. \quad (4.13.21)$$

On the basis of our computations, the factor $1 + md \log f/dm$ should be responsible for the variation of the diffusion coefficient of D with concentration, and we may expect that D will assume a minimum value at some concentration in the range 0.1-1n., say, corresponding to the minimum of (4.13.21).

For an experimental test of our predictions, direct measurements of the differential coefficient of diffusions are preferable. Such measurements have been carried out in relatively recent times by B. W. Clack[2] who enployed an interferometric method. Most experimenters have been content to measure the rate at which a given solution diffuses against pure solvent; this procedure

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[1] Hückel: Physik. Z., 26, 93 (1925). Formulas (100) together with (27a) and (30), the latter for conversion of concentrations.

[2] B. W. Clack: Proc. Phys. Soc. London, 36, 313 (1929).

yields a sort of an average coefficient of diffusion for all intermediate concentrations, and the type of averaging depends on the time when the experiment is interrupted for analysis. We have compared some of Öholm's data[1] with appropriate averages of our calculated D values. His results carry some resemblance to the theoretical predictions, but in several cases (KCl, NaCl), an extrapolation of his data leads to a limiting D value which is definitely higher than that computed from electrolytic mobilities, and we do not know how to interpret this discrepancy. We might mention in this connection that Öholm's measurements were performed at temperatures ranging all the way from 4°C. up to 18°, and were reduced to 18° by temperature coefficients. However, it is our impression that the discrepancy in extrapolation cannot be ascribed to an error in the temperature coefficients, because at higher concentrations Öholm's values agree substantially with those given by Clack. In the particular case of HCl, Öholm's D values extrapolate "correctly" and conform to the theory over a range of concentrations from 0.003 n. to 0.06 n. but it is not fair to select the most favorable case. We shall be content to state that reasonable inference from Öholm's data, to the extent that we have studied them, does not alter the picture which we shall presently derive from Clack's observations.

Clack measured the coefficients of diffusion for NaCl, KCl and KNO_3 over a range of concentration from 0.05 n. to saturation. While a lowest concentration of 0.05 n. does not permit a test of our "limiting laws," our calculations show that the Coulomb forces ought not (greatly) affect Ω/m very much at any concentration, which justifies a consideration of experimental data even for relatively concentrated solutions. For NaCl and KCl, but not for KNO_3, accurate measurements of the thermodynamic potentials by e.m.f. are available. Harned[2] found that his data could be represented very well by Hückel's formula (4.13.20); the following values for the constants A and B were derived from his data:

$$\begin{aligned} &\text{NaCl: } A = 0.84;\ B = 0.129;\ a = 3.62 \times 10^{-8}\text{ cm.} \\ &\text{KCl: } \ \ A = 0.76;\ B = 0.071;\ a = 3.28 \times 10^{-8}\text{ cm.} \end{aligned} \qquad (4.13.22)$$

These values are valid for 25°, while Clack's diffusion experiments were made at 18°; the difference, which can be estimated from heats of dilution[3] is negligible for our purposes. For the calculation of Ω/m, the values of A given by Harned were adopted; hence for KCl

$$10^{20}\,\Omega/m = 34.84 + 15.6\,m\,\varphi(0.76\sqrt{m})$$

and for NaCl

$$10^{22}\,\Omega/m = 28.01 - 0.39\,\frac{\sqrt{2m}}{1 + 0.84\sqrt{2m}} + 15.6\,m\,\varphi(0.84\sqrt{2m}).$$

The results of these calculations are represented in Fig. 7. The curve for KCl is simply a graph of the function $\varphi(\kappa a)$. In Fig. 8, the solid curves are the calculated values for the coefficient of diffusion (in units cm^2/sec.), while circles

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[1] Öholm: Z. physik. Chem., **50**, 309 (1904); **70**, 378 (1910).

[2] Harned: J. Am. Chem. Soc., **51**, 416 (1929).

[3] Wüst and Lange: Z. physik. Chem., **116**, 161 (1924).

and crosses indicate different runs in Clack's experiments. The general type of the relation between D and concentration is accounted for by the theory, and for the lowest concentrations the agreement between theory and experiment is satisfactory. As regards the theoretical predictions for the variation of Ω/m with concentration, the confirmation is only negative, that is, the experiments show that for low concentrations, Ω/m does not vary much more than predicted by the theory.

At higher concentrations, we meet with quite appreciable deviations, particularly in the case of NaCl, and our theory for Ω/m is definitely not adequate.

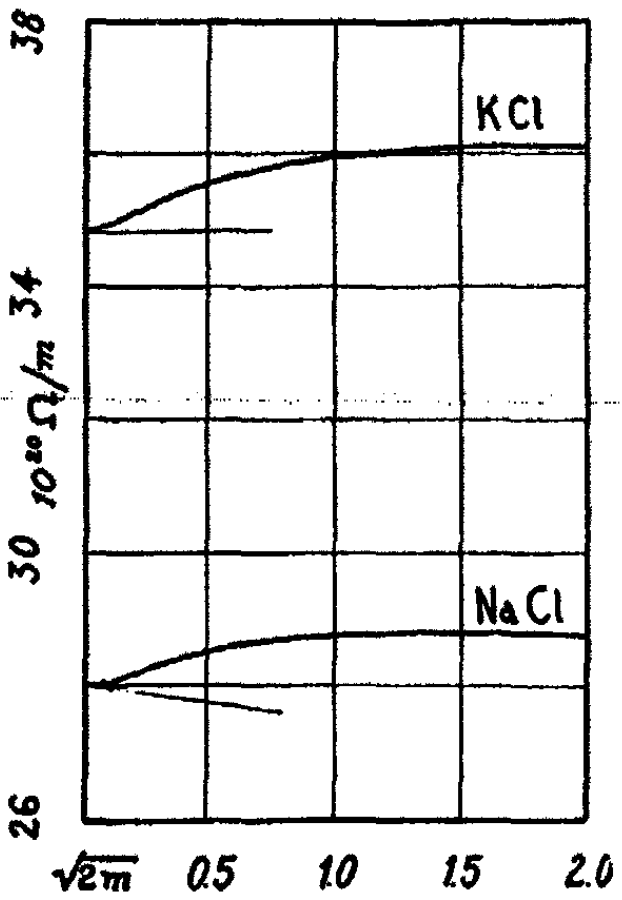

FIG. 7

Dependence of Mobility Ω/m on Concentration

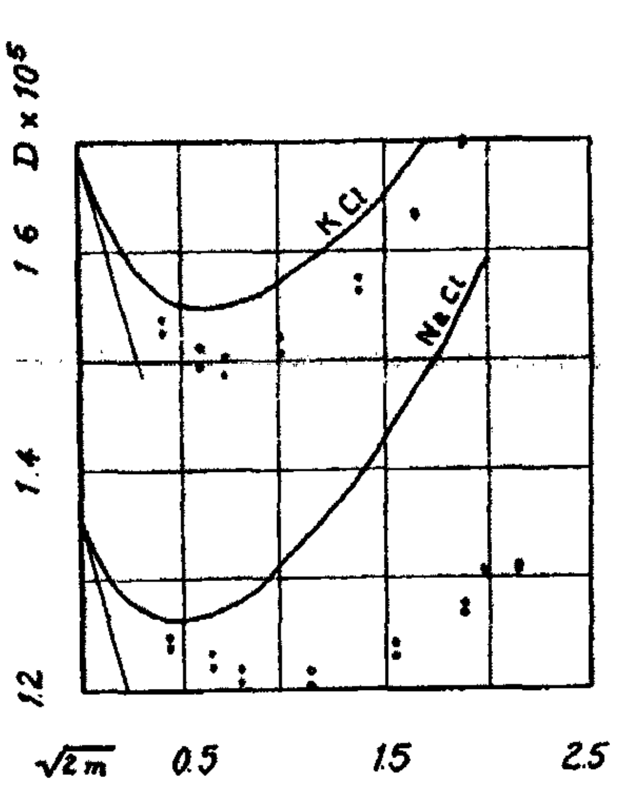

FIG. 8

Dependence of Coefficient of Diffusion on Concentration

The discrepancy is too large to be ascribed to Coulomb forces between the ions; while our calculations are admittedly not accurate for concentrated solutions, at least the order of magnitude of the effects due to these forces should be correctly computed. The differences between calculated and observed values for D are nearly linear functions of m, indicating that they are probably due to specific properties of the electrolytes, which have not been allowed for in the calculations. We suspect two effects, namely viscosity and "hydration." At 1 n. concentration, the difference (calc. − obs.) amounts to 3.4% (of calc.) in the case of KCl, and 12.5% in the case of NaCl. The fluidity of 1 n. KCl is 1.018, that of 1 n. NaCl is 0.921, reckoned to unity for pure solvent.[1]

If the mobility is assumed proportional to the first power of fluidity, we obtain residual defects in D of around 5.2% for KCl and 4.6% for NaCl (at

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[1] These figures are computed from macroscopic viscosities, which contain an electrostatic contribution that should actually be subtracted in calculating the "microscopic" viscosity that applies to ions; but the difference is too small to be important here.

1 n. concentration); this defect must be attributed to other causes, e.g. hydration. A fractional power of the fluidity may be more appropriate;[1] in that event, the residual effect for KCl becomes smaller, that for NaCl greater.

In using the term "hydration," we shall not necessarily imply that a given ion has a definite number of solvent molecules firmly attached, but merely that there exists a region surrounding each ion, in which other ions are relatively scarce. For a simplified picture we might assume a "forbidden" region around each ion. We have tried to estimate the "forbidden" volume from the values of A and B in (4.13.22), and obtained values of the order 10^{-22} cm^3, which corresponds to a few (3) molecules of solvent. A hydration of one molecule of solvent per ion, firmly bound, (or maybe a couple loosely bound), would decrease Ω/m by 3.6%, (that is $100 \times 2 \times 18.03/1000$) at 1 n. concentration. On this basis it seems quite plausible that defects of the order 5%, as found above, can be attributed to hydration. At the same time, it becomes apparent that an exact computation would require an exceedingly detailed knowledge of concentrated electrolytes.

4.14. *The Dissipation-Function for a Simple Electrolyte.*

So far, we have consistently sought formulas which gave the velocities of the ions explicitly by the forces. For certain purposes, particularly for a simple formulation of the laws for combined conduction and diffusion, it is more convenient to express the "forces" by the velocities, as follows:

$$- \operatorname{grad} \mu_j = \mathbf{k}_j = \sum_{\sigma=1}^{s} R_{j\sigma} \mathbf{J}_\sigma \qquad (4.14.1)$$

In the limit of very low concentrations, only the friction of the solvent need be considered, so that

$$\mathbf{k}_j = \rho_j \mathbf{v}_j = \mathbf{v}_j/\omega_j = \mathbf{J}_j/n_j\omega_j. \qquad (4.14.2)$$

At finite concentrations, the electrostatic interaction of the ions must be taken into account; hence

$$\mathbf{k}_j = \rho_j \mathbf{v}_j - e_j \Delta X_j - \rho_j \Delta \mathbf{v}_j, \qquad (4.14.3)$$

where ΔX_j is the electric field on an ion due to its atmosphere, and $\Delta \mathbf{v}_j$ is the electrophoretic flow of the medium surrounding an ion, which adds $-\Delta \mathbf{v}_j$ to the relative velocity of the ion with respect to the surrounding solution.

For the case of a simple electrolyte ($s = 2$), it is possible to derive fairly simple explicit formulas, as we have in effect done above. In order to calculate the ionic field, we start conveniently with the general formula

$$- \Delta X_j = \operatorname{grad} \psi'_j (0) = \frac{1}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \sqrt{n_\sigma \omega_\sigma}\, e_\sigma \mathbf{k}_\sigma, \qquad (4.6.4)$$

(summation-sign omitted). The symmetrical matrix $\kappa.1 - K^{1/2}$ may be expanded in terms of its eigenvectors:

$$(\kappa - K^{1/2})_{ji} = \sum_{\sigma=1}^{s} (\kappa - \sqrt{\alpha_\sigma})\, l_{\sigma j} l_{\sigma i}, \qquad (4.14.4)$$

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[1] This suggestion has been made by other authors for the interpretation of data on conductance.

where $\alpha_1, \ldots, \alpha_s$ are the eigenvalues, and $l_1, \ldots, l_s$ the corresponding eigenvectors of K. We have shown (§ 3.8) that for our matrix K always

$$\kappa^2 = \alpha_1 > \alpha_2 \geq \ldots \geqslant \alpha_s > 0, \tag{3.8.4}$$

$$l_{1j} = e_j \sqrt{n_j \rho_j / n_\sigma e_\sigma^2 \rho_\sigma}. \tag{3.8.5}$$

For $s = 2$, we obtain simply

$$(\kappa - K^{1/2})_{ji} = (\kappa - \sqrt{\alpha_2})\, l_{2j} l_{2i}. \tag{4.14.5}$$

For this particular case (2 dimensions) an orthogonal matrix (l_{ik}) represents a rotation in the plane and has the form

$$\begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix},$$

so that

$$\begin{aligned} l_{21} &= -l_{12} = -e_2\sqrt{n_2\omega_1/(n_1e_1^2\omega_2 + n_2e_2^2\omega_1)} \\ l_{22} &= l_{11} = e_1\sqrt{n_1\omega_2/(n_1e_1^2\omega_2 + n_2e_2^2\omega_1)}. \end{aligned} \tag{4.14.6}$$

We have also seen that for the case $s = 2$,

$$\alpha_2 = q\kappa^2 = \frac{n_1e_1^2\omega_1 + n_2e_2^2\omega_2}{(n_1e_1^2 + n_2e_2^2)(\omega_1 + \omega_2)}\, \kappa^2. \tag{3.8.29}$$

Substituting these formulas in (4.6.4), we obtain

$$\Delta X = \Delta X_1 = \Delta X_2 = \frac{\kappa(1 - \sqrt{q})}{3DkT} \frac{e_1e_2(n_2e_2)}{n_1e_1^2\omega_2 + n_2e_2^2\omega_1} (\omega_2\mathbf{k}_2 - \omega_1\mathbf{k}_1). \tag{4.14.7}$$

We note again that ΔX is proportional to $\sqrt{n}$ (with κ), where n is the concentration. From its derivation, (4.14.7), like our other main results, expresses an asymptotic law, and powers of n higher than $n^{1/2}$ have been neglected. In calculating this "first order" term, we may substitute the "zero order" approximation (4.14.2) for $\mathbf{k}_1$ and $\mathbf{k}_2$, as follows:

$$n_2e_2(\omega_2\mathbf{k}_2 - \omega_1\mathbf{k}_1) = n_2e_2(\mathbf{v}_2 - \mathbf{v}_1) = n_2e_2\mathbf{v}_2 + n_1e_1\mathbf{v}_1 = e_1\mathbf{J}_1 + e_2\mathbf{J}_2. \tag{4.14.8}$$

It is seen that the ionic field ΔX is proportional to the velocity difference between anions and cations.

The electrophoretic correction we take from (4.2.15), omitting the "second order" term with $\varphi(\kappa a)$; thus

$$n_j\, \Delta\mathbf{v}_j = -\frac{2}{3\eta\kappa DkT}\, n_j\, e_j \Sigma\, n_\sigma e_\sigma \mathbf{k}_\sigma$$

or, with the approximation (4.14.2) for $\mathbf{k}_1$ and $\mathbf{k}_2$:

$$-\rho_j\Delta\mathbf{v}_j = \frac{2}{3\eta\kappa DkT}\, e_j\rho_j\, \Sigma\, e_\sigma\rho_\sigma\mathbf{J}_\sigma. \tag{4.14.9}$$

We substitute this formula together with (4.14.7-8) in (4.14.3), and obtain

$$\begin{aligned} \mathbf{k}_j = \frac{\rho_j}{n_j}\mathbf{J}_j &+ \frac{\kappa}{3DkT}\frac{(-e_1e_2)(1 - \sqrt{q})}{(n_1e_1^2\omega_2 + n_2e_2^2\omega_1)}\, e_j(e_1\mathbf{J}_1 + e_2\mathbf{J}_2) \\ &+ \frac{2}{3\eta\kappa DkT}\, e_j\rho_j(e_1\rho_1\mathbf{J}_1 + e_2\rho_2\mathbf{J}_2). \end{aligned} \tag{4.14.10}$$

By comparison with (4.14.1) it is seen that the reciprocal relation

$$R_{12} = R_{21}$$

holds. We may then write (4.14.10) in the form

$$\mathbf{k}_j = \partial F/\partial \mathbf{J}_j, \tag{4.14.11}$$

with the *dissipation-function*

$$2F = R_{11}\mathbf{J}_1^2 + 2R_{12}\mathbf{J}_1\mathbf{J}_2 + R_{22}\mathbf{J}_2^2 = (\mathbf{J}_1^2/n_1\omega_1) + (\mathbf{J}_2^2/n_2\omega_2)$$
$$+ \frac{-e_1e_2\kappa}{3DkT}\frac{(1-\sqrt{q})}{(n_1e_1^2\omega_2 + n_2e_2^2\omega_1)}(e_1\mathbf{J}_1 + e_2\mathbf{J}_2)^2 +$$
$$\frac{2}{3\eta\kappa DkT}(e_1\rho_1\mathbf{J}_1 + e_2\rho_2\mathbf{J}_2)^2. \tag{4.14.12}$$

The ionic field and the electrophoresis both cause positive contributions to the dissipation-function. The former vanishes when all ions migrate with the same velocity, which in the case of a simple electrolyte means no electric current. The additional dissipation due to electrophoresis vanishes when

$$e_1\mathbf{J}_1\rho_1 + e_2\rho_2\mathbf{J}_2 = n_1e_1(\mathbf{v}_1\rho_1 - \mathbf{v}_2\rho_2) = 0,$$

that is, when anions and cations meet the same frictional resistance per ion, (both migrating in the same direction).

When the theory is elaborated to include in the dissipation-function terms of higher order than $\sqrt{n}$ for instance $n \log n$, the picture becomes more complicated. While we have made no exhaustive search for terms of any order higher than the first, we may point out that the second order term in formula (4.2.15) for the electrophoretic effect will lead to the *negative* term

$$-\frac{\varphi(\kappa a)}{3\eta(DkT)^2}(e_1^2\rho_1\mathbf{J}_1 + e_2^2\rho_2\mathbf{J}_2)_2$$

in the dissipation-function.

4.15. *Diffusion of a General Electrolyte.* *Dissipation-function.*

Diffusion in a system containing three or more ions is a subject of considerable interest. The case which has received the most attention is the interdiffusion of two different electrolytes; both the rates of diffusion and, particularly, the electromotive forces at the boundary have been studied. Unfortunately, the equations of diffusion for such cases are very difficult to integrate even when the variation of activity coefficients and mobilities with concentration is neglected. The velocities of the ions 1, . . ., s are determined by the gradients of concentration, $n_1 \ldots n_s$, subject to the condition of electric neutrality

$$\sum_i n_ie_i = 0, \tag{4.15.1}$$

and by the electric field; the latter automatically adjusts itself so that the solution remains electrically neutral everywhere in accord with (4.15.1).

When the effects of Coulomb forces between the ions are neglected, (except the macroscopic electric field, which depends on space charges in the electrolyte), the equations of diffusion are for a one-dimensional case (parallel flow)

$$\mathbf{J}_i = \omega({}_i n_i e_i \mathbf{X} - kT\,\partial n_i/\partial x) \qquad (4.15.2)$$

together with (4.15.1). The electric field is related to the current density

$$\mathbf{i} = \sum_i e_i \mathbf{J}_i$$

by the equation

$$\lambda \mathbf{X} = \mathbf{i} + kT \sum_i e_i \omega_i \partial n_i/\partial x, \qquad (4.15.3)$$

where λ denotes the specific conductance of the solution:

$$\lambda = \sum_i n_i e_i^2 \omega_i.$$

The integration on (4.15.2) and (4.15.3) cannot be carried out in closed form except in certain special cases, most of which are trivial. The one case of interest which can be conveniently computed is the interdiffusion of two electrolytes (mixtures) of nearly the same composition,[1] determined by the differential coefficients of diffusion for the given (nearly constant) composition. The computation of this special case is feasible because $n_1 \ldots n_s$ may be considered (for a first approximation) as constant coefficients in a system of equations involving $\partial n_1/\partial x, \ldots, \partial n_s/\partial x$, linear in the latter. If necessary, the variation of $n_1 \ldots n_s$ may be taken into account by successive approximations.

The simple theory demands that the differential coefficients of diffusion should depend only on the *ratios* of $n_1 \ldots n_s$ and remain constant when the concentrations are varied in proportion. When the interionic forces are taken into account, this simple relation no longer holds; our object is to calculate the corrections.

We shall develop differential equations which allow for the Coulomb forces between the ions, and discuss the most important relations to the underlying physical picture. For eventual applications, it would be necessary to integrate our final equations, which is again feasible for the case of *differential* diffusion, as outlined above. As long as no actual measurements of this type are available, we have not found it worth labor and space to carry out these integrations.

We employ the general form (4.12.8)

$$\mathbf{k}_i = -\operatorname{grad} \mu_i = \sum_{k=1}^{s} R_{ik} \mathbf{J}_k, \qquad (4.15.4)$$

with the convention (4.12.15), that the electric field X is included in grad μ, thus:

$$-\operatorname{grad} \mu_i = -\operatorname{grad} \mu_i' + e_i X.$$

The splitting of grad μ_i into an electrical part $e_i X$ and a "chemical" part grad μ_i' has been discussed in § 4.12. As shown there, the concentration

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[1] For example, one solution containing KCl (0.050 N) and HCl (0.030 N), and another containing KCl (0.050 N) and HCl (0.028 N).

gradients yield $n-1$ relations to determine grad $\mu_1, \ldots,$ grad μ_s; the nth relation necessary to complete the determination is derived from the condition of electric neutrality (4.15.1), which again leads to

$$\Sigma\, e_i\, \partial n_i/\partial t = -\operatorname{div} \Sigma\, e_i\mathbf{J}_i = -\operatorname{div} \mathbf{i} = 0,$$

or in the case of parallel flow:

$$-\sum_i e_i \sum_k \Omega_{ik}\, \partial\mu_k/\partial x = \sum_i e_i\mathbf{J}_i = \mathbf{i} = \text{const.} \qquad (4.15.5)$$

where $\mathbf{i}$ is the electric current.

The case of "pure diffusion" is defined by $\mathbf{i} = 0$, for our purposes a specialization of no important consequence, except that it is common in practice.

We employ the general formula (4.14.3)

$$\mathbf{k}_j = \rho_j\mathbf{v}_j - e_j\Delta\mathbf{X}_j - \rho_j\Delta\mathbf{v}_j, \qquad (4.15.6)$$

where the terms on the right represent, in the order named, the friction of the ion against the solvent, the asymmetric electric field of the atmosphere, and the electrophoretic velocity at the centre of the atmosphere. We can calculate the latter as in the preceding section (4.14.9), thus

$$-\rho_j\Delta\mathbf{v}_j = \frac{2}{3\eta\kappa DkT}\, e_j\rho_j \sum_\sigma e_\sigma\rho_\sigma\, \mathbf{J}_\sigma = R'_{j\sigma}\mathbf{J}_\sigma. \qquad (4.15.7)$$

For the ionic field, we use the formula

$$-\Delta X_j = \operatorname{grad} \psi'_j(0) =$$

$$= \frac{1}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \sqrt{n_\sigma\omega_\sigma}\, e_\sigma\mathbf{k}_\sigma, \qquad (4.6.4),$$

or, substituting the "zero approximation"

$$\mathbf{k}_i = \mathbf{v}_i/\omega_i = \mathbf{J}_i/n_i\omega_i$$

for the force,

$$-e_j\Delta X_j = \frac{e_j}{3DkT\sqrt{n_j\omega_j}} (\kappa - K^{1/2})_{j\sigma} \frac{e_\sigma}{\sqrt{n_\sigma\omega_\sigma}} \mathbf{J}_\sigma = R''_{j\sigma}\mathbf{J}_\sigma. \qquad (4.15.8)$$

Now if we write

$$R_{ji} = (\rho_j/n_j)\, \delta_{ji} + R'_{ji} + R''_{ji}$$

where R'_{ji} and R''_{ji} are given by (4.15.7-8), we have from (4.15.6)

$$\mathbf{k}_j = R_{j\sigma}\, \mathbf{J}_\sigma = (\rho_j/n_j)\, \mathbf{J}_j + (R'_{j\sigma} + R''_{j\sigma})\, \mathbf{J}_\sigma. \qquad (4.15.9)$$

Here we shall point out in the first place that the matrix R is symmetrical, as required by (4.12.9). The first term in (4.15.9) is diagonal; R'_{ji} is symmetrical according to (4.15.7), and R''_{ji} likewise according to (4.15.8), on account of the symmetry of the matrix K.

The dissipation function takes the form

$$2\,F(\mathbf{J},\mathbf{J}) = \Sigma\Sigma\, R_{ji}\,\mathbf{J}_j\,\mathbf{J}_i =$$

$$= \Sigma \frac{\rho_j}{n_j}\mathbf{J}_j^2 + \frac{2}{3\eta\kappa DkT}(\Sigma e_j\,\rho_j\mathbf{J}_j)^2 + \frac{1}{3DkT}\left(\sum_j \frac{e_j^2\kappa}{n_j\,\omega_j}\mathbf{J}_j^2 - \sum_{j,i}\frac{K^{1/2}{}_{ji}\,e_j\,e_i}{\sqrt{n_j\,n_i\,\omega_j\,\omega_i}}\mathbf{J}_j\,\mathbf{J}_i\right) \qquad (4.15.10)$$

The fundamental equations for combined conduction and diffusion are

$$-\operatorname{grad}\mu_i = \partial F/\partial\mathbf{J}_i = \sum_k R_{ik}\,\mathbf{J}_k. \qquad (4.15.11)$$

In the dissipation-function (4.15.10), the electrophoretic contribution (second term) consists of a single squared term. The contribution from the ionic fields $2\,F'' = \Sigma R''_{ji}\,\mathbf{J}_j\,\mathbf{J}_i$, contains s-1 squared terms, which is the number of positive characteristic numbers of the quadratic form

$$\kappa\,\Sigma x^2 - K^{1/2}\,(x, x) = \sum_{p=1}^{s}(\kappa - \sqrt{\alpha_p})\,(\sum_i l_{pi}\,x_i)^2,$$

where according to (3.8.4),

$$\kappa^2 = \alpha_1 > \alpha_2 \geqslant \ldots \geqslant \alpha > 0.$$

This implies that F'' will vanish for a certain not trivial set of values of $\mathbf{J}_1, \ldots, \mathbf{J}_s$, corresponding to the eigenvector l_1, of K. From (3.8.5), it is easily verified that F'' vanishes when

$$\mathbf{J}_1/n_1 = \mathbf{J}_2/n_2 = \ldots = \mathbf{J}_s/n_s = \mathbf{v}_1 = \mathbf{v}_2 = \ldots = \mathbf{v}_s,$$

that is, when the velocities of all ions are equal. This is what we should expect, because a simultaneous displacement of all ions will not disturb the ionic atmospheres. We may, therefore, if we like, express F'' in the alternative form

$$2F'' = -\tfrac{1}{2}\sum_{j,i} R''_{ji}\,n_j\,n_i\,(\mathbf{v}_j - \mathbf{v}_i)^2, \qquad (4.15.12)$$

which is the same as $\sum_{j,i} R''_{ji}\mathbf{J}_j\mathbf{J}_i$ because, as is readily verified with the aid of (3.8.5)

$$\sum_i n_i R''_{ji} = \sum_i n_i R''_{ij} = 0.$$

The construction of the electrophoretic term F′ in (4.15.10) is apparent on sight; but some interesting properties of F″ are hidden. We shall next show that F'', the contribution to the dissipation function arising from the interaction of the ionic fields, is proportional to the 3/2 power of the total ionic strength Γ and that the proportionality factor is determined by the velocities $\mathbf{v}_1, \ldots \mathbf{v}_s$, the mobilities $\omega_1, \ldots, \omega_s$, and the ratios of ionic strengths $\mu_1, \ldots, \mu_s$. We have for $2F''$, according to (4.5.10),

$$2F'' = \sum_j\sum_i R''_{ji}\,\mathbf{J}_j\,\mathbf{J}_i = \mathbf{J}_\sigma R''_{\sigma\tau}\,\mathbf{J}_\tau =$$

$$= \frac{\kappa}{3DkT}\sqrt{n_\sigma\,\rho_\sigma}\,e_\sigma\,\mathbf{v}_\sigma\,(1 - \kappa^{-1}K^{1/2})_{\sigma\tau}\sqrt{n_\tau\,\rho_\tau}\,e_\tau\,\mathbf{v}_\tau. \qquad (4.15.13)$$

We now recall the transformation (4.7.5):

$$M^{-1}f(\kappa^{-2}K)\,\mathrm{M} = \kappa^{-2}f(G) = f(H),\ m_{ji} = \delta_{ji}\,e_j\sqrt{n_j\,\omega_j} \qquad (4.7.5)$$

$$h_{ji} = \delta_{ji}\sum_i \mu_i \frac{\omega_i}{\omega_i+\omega_j} + \mu_i \frac{\omega_i}{\omega_i+\omega_j} \qquad (4.7.7)$$

by means of which we introduced a matrix H where the elements are all pure numbers. On applying (4.7.5) to (4.15.13), we obtain

$$2F'' = \frac{\kappa}{3DkT}\,n_\sigma\,e_\sigma^2\,\mathbf{v}_\sigma\,(1 - H^{1/2})_{\sigma\tau}\,\mathbf{v}_\tau\,\rho_\tau$$

and on substituting (4.7.1-3),

$$2F'' = \left(\frac{N\epsilon^2}{1000\,k}\right)^{3/2}\frac{2\sqrt{\pi}}{3}\left(\frac{\Gamma}{DT}\right)^{3/2}\mu_\sigma\,\mathbf{v}_\sigma\,(1 - H^{1/2})_{\sigma\tau}\,\mathbf{v}_\tau\,\rho_\tau. \qquad (4.15.14)$$

Numerical computation by means of (4.15.14) is made by a procedure parallel to that developed in § 4.7 for the conductance problem; there is no need to repeat the manipulation here. In (4.15.14), the concentrations of the various ionic species appear only as the ratios $\mu_j = \Gamma_j/\Gamma$, while the total concentration is represented by the factor $\Gamma^{3/2} = (m_\sigma z_\sigma^2)^{3/2}$. The mobilities enter in the elements of H, by their ratios, (cf. 4.7.7), and in the vector with components $\mathbf{v}_j\,\rho_j$ representing the force on an ion.

It is of interest to compute the dissipation function for a special case, corresponding to equal mobilities

$$\omega_1 = \omega_2\ \ldots = \omega_s = \omega = 1/\rho,$$

because the nature of the various terms of (4.15.10) is then very readily seen. For this case, the term 2F″ simplifies to

$$2F'' = \frac{\kappa\rho}{3DkT}\sqrt{n_\sigma}\,e_\sigma\,\mathbf{v}_\sigma\,(1 - \kappa^{-1}K^{1/2})_{\sigma\tau}\sqrt{n_\tau}\,e_\tau\,\mathbf{v}_\tau,$$

which may be written in terms of a quadratic form $C(x, x)$,

$$2F'' = \frac{\kappa\rho}{3DkT}\,C(\sqrt{n}\,e\,\mathbf{v},\ \sqrt{n}\,e\,\mathbf{v}). \qquad (4.15.15)$$

The form $C(x, x)$ is easily determined because the elements of $\kappa^{-2}K$ reduced to

$$\kappa^{-2}k_{ji} = \tfrac{1}{2}\,\delta_{ji} + \frac{e_i\,e_j\sqrt{n_i\,n_j}}{2\,n_\sigma e_\sigma^2}.$$

The second term contains only the eigenvector l_1 (cf. (3.8.5)), thus

$$\kappa^{-2}k_{ji} = \tfrac{1}{2}\,\delta_{ji} + \tfrac{1}{2}\,l_{1j}\,l_{1i}.$$

Then we have for the quadratic form $\mathrm{K}(x, x)$ in this special case

$$K(x, x) = \kappa^2\,(l_{1\sigma}\,x_\sigma)^2 + \sum_{p=0}^{s}\tfrac{1}{2}\,\kappa^2\,(l_{p\sigma}\,x_\sigma)^2,$$

so that the characteristic numbers are

$$\alpha_1 = \kappa^2, \alpha_2 = \alpha_3 = \, . \, . \, . \, . = \alpha_s = \kappa^2/2.$$

Then $C = (1 - \kappa^{-1} K^{1/2})$ has the same eigenvectors and the characteristic numbers

$$\xi_1 = 0, \xi_2 = \xi_3 = \, . \, . \, . = \xi_s = 1 - \sqrt{1/2} = (2 - \sqrt{2})/2$$

and

$$C(x, x) = \frac{2 - \sqrt{2}}{2} (x_\sigma^2 - (l_{1\sigma} x_\sigma)^2). \tag{4.15.16}$$

Substituting (4.15.16) in (4.15.15), we obtain

$$2F'' = \frac{\kappa\rho(2 - \sqrt{2})}{6DkT} \left\{ \sum_i n_i e_i^2 \mathbf{v}_i^2 - \left(\frac{\sum_i \sqrt{n_i}\, e_i \sqrt{n_i}\, e_i \mathbf{v}_i}{(\sum_k n_k e_k^2)^{1/2}} \right)^2 \right\} \tag{4.15.17}$$

$$= \frac{2 - \sqrt{2}}{6} \frac{\kappa\rho}{DkT} \sum_i n_i e_i^2 (\mathbf{v}_i - \bar{\mathbf{v}})^2,$$

where

$$\bar{\mathbf{v}} = n_\sigma e_\sigma^2 \mathbf{v}_\sigma / n_\tau e_\tau^2$$

denotes the average velocity of the atmosphere. Hence, when the coefficients of diffusion, $(kT \omega)$ are the same for all ions, the entire dissipation-function takes the form

$$2 F(\mathbf{v}, \mathbf{v}) = \rho \sum_i n_i \mathbf{v}_i^2 + \frac{2\rho}{3\eta\kappa DkT} (\sum_j n_j e_j \mathbf{v}_j)^2$$

$$+ \frac{2 - \sqrt{2}}{6} \frac{\kappa\rho}{DkT} \sum_j n_i e_i^2 (\mathbf{v}_i - \bar{\mathbf{v}})^2. \tag{4.15.18}$$

The first term on the right is the contribution to entropy production (energy dissipation) due to the frictional forces of the ions against the solvent. The second term represents the contribution due to the electrophoretic effect, and is approximately independent of the viscosity of the solvent, because the ratio $\eta/\rho \sim$ ionic radius enters. (cf. (4.2.4)). The last term is the effect produced by the assymetry of the ionic fields, and as might be suspected, depends on the differences in mobility of the various ionic species present.

5. Summary

1. The effects of the Coulomb forces between ions on *transport processes,* namely: diffusion, electrolytic conduction, and viscous flow are considered from a common point of view.

2. It is shown how results previously obtained for simple electrolytes can be extended to mixtures containing an arbitrary number of ionic species, and general limiting laws are derived. *As in the case of simple electrolytes, the* electrostatic effects are *proportional to the square root of concentration.*

3. The fundamental equations of the ionic atmospheres lead to systems of differential equations which are compactly treated by *matrix algebra*. The *numerical* evaluation of the formal results is illustrated by examples.

4. The electrostatic contribution to *viscosity* is computed explicitly for the general case, and some simple special cases are discussed in more detail. The mechanism of *force transfer* is investigated.

5. The general limiting laws for *conduction in mixtures* are derived. Kohlrausch's rule of the independent migration of ions, valid as a limiting law for simple binary electrolytes, does not apply to mixtures, nor are the conductances additive. The computed deviations are compared with experiment.

6. The *general laws of diffusion* are discussed with particular reference to electrolytes. The effects of the Coulomb forces are computed for simple electrolytes and for mixtures. The theoretical results for the former are compared with the available data.

7. The rate of production of entropy in transport processes is a quadratic function of the velocities. With the aid of this *dissipation-function*, the laws of combined diffusion and electric conduction are formulated and discussed.

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FLUORINE POLYHALIDES*

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Introduction

Many polyhalides of the various elements, chiefly of the alkali metals of the first group, have been prepared. Numerous methods have been used to prepare the polyhalides, and there is question as to whether or not some that are said to exist really do. But chemists seem to have forgotten that fluorine is a halogen; all of the studies have been made on the polyhalides containing chlorine, bromine, and iodine, in various combinations and proportions. Perhaps the reason for this apparent oversight of fluorine has been the aversion of chemists to the handling of fluorine and the fluorides.

According to Sidgwick,[1] "Any halogen except fluorine can form part of a perhalide." He assumes that fluorine does not follow the behavior peculiar to the polyhalide formation because it is the lightest halogen and only the heavier ones follow this rule.

The purpose of this paper is to describe the preparation of the salts formed by the union of iodine trichloride and the fluorides of the alkali metals, cesium, rubidium, potassium, and ammonium, their properties and the experimental data for the preparation and analyses of the salts.

Historical

It has long been known that iodine would dissolve in potassium iodide solutions, either alcoholic or aqueous, but it was not known whether it was merely a physical solution or whether a complex polyhalide of potassium was formed. There was some evidence for both lines of reasoning. Baudrimont[2] found that carbon disulfide removed the iodine dissolved in an aqueous solution of potassium iodide. This would indicate that no chemical compound was formed. Jorgensen[3] said that carbon disulfide did not remove iodine from an alcoholic solution of potassium iodide containing two atomic weights of iodine for each atomic weight of potassium iodide. He also showed that an alcoholic solution of potassium iodide completely removed the iodine from a solution of it dissolved in carbon disulfide. This would indicate that a compound was formed by the iodine uniting with the potassium iodide.

Since this early work there have been many complex halides isolated containing not only iodine but also chlorine and bromine. All of the polyhalides

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[1] Sidgwick: "The Electronic Theory of Valence," 293 (1927).

[2] Baudrimont: Compt. rend., 51, 825 (1860).

[3] Jorgensen: J. prakt. Chem., 2, 347 (1870).

that have been prepared may be divided into two major classes; those containing three halogen atoms and those containing five halogen atoms. Table I contains a list of all of the alkali metal polyhalides, arranged in the order of increasing stability. This stability is based on the temperature to which it is necessary to heat the compound in an open tube before it whitens. In general the stability is as follows: $Cs > Rb > NH_4 > K > Na > Li$.

Trihalides

By concentrating an aqueous or alcoholic iodine-potassium iodide solution over sulfuric acid in a desiccator Johnson[1] obtained some large, dark blue, prismatic crystals which he claimed, from the result of his analyses, to be potassium triiodide. Wells[2] and some of his co-workers repeated Johnson's preparation but not the analysis.

Abegg and Hamburger[3] attempted to determine the composition of all the alkali polyiodides that are stable at 25°C. by shaking the solid iodide in varying amounts of a nearly saturated solution of iodine in benzene. They found no evidence of the compound KI_3. Several phase rule studies of the system KI-I_2-H_2O have been made but none of them even indicated that KI_3 existed. Bancroft[4] made a phase-rule study of the system and found no evidence for the existence of KI_3. On repeating Johnson's work he obtained the same salt and, by using the same inaccurate method of analysis that Johnson used, he found that the iodine content of the salt corresponded with that required for KI_3. On making an X-ray study of the salt he found that there was no indication that the salt was potassium tri-iodide. Bancroft concluded from his study of the salt that it was merely potassium iodide that had taken up enough iodine to change its crystal structure slightly and to give the analysis corresponding to KI_3.

Briggs and Geigle[5] made a freezing point study of various mixtures of potassium iodide and iodine and found that potassium iodide and iodine were the only solids that could exist in equilibrium with the melt.

Serullas[6] prepared potassium dichloro-bromide and potassium dibromochloride by the action of chlorine monobromide on potassium chloride and potassium bromide. Abegg and Hamburger (loc. cit) found evidence for the existence of RbI_3, CsI_3, and NH_4I_3. Foote and Chalker[7] claim to have isolated the tri-iodides of cesium, rubidium, and potassium. Wells and Wheeler (loc. cit.) have prepared the following trihalides in addition to the potassium triiodides: $CsBrI_2$, $CsBr_2I$, $CsClBrI$, $CsCl_2I$, $CsBr_3$, $CsClBr_2$, $CsCl_2Br$, CsI_3, RbI_3, $RbBr_2I$, $RbClBrI$, $RbBr_3$, $RbCl_2Br$, $RbClBr_2$, KBr_2I, and KCl_2I by dissolving the normal halide and the halogen in question in a warm water or

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[1] Johnson: J. Chem. Soc., 31, 249 (1877).

[2] Wells: "Studies from the Chemical Laboratory, Sheffield Scientific School," Vol. I, Inorganic Chemistry.

[3] Abegg and Hamburger: Z. anorg. Chem., 50, 427 (1906).

[4] Bancroft: J. Phys. Chem., 35, 764 (1931).

[5] Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930).

[6] Serullas: Ann. Chim. Phys., 45, 190 (1830).

[7] Foote and Chalker: Am. Chem. J., 39, 561 (1908).

weak alcohol solution. They were unable to prepare the other trihalides necessary to complete the series. The colors range from brilliant black for CsI_3 to bright yellow for $CsCl_2Br$. They found that the trihalides containing iodine were more stable than those not containing iodine, but that the instability of the compound was not governed entirely by the volatility of the halogen, for they found that $CsCl_2Br$ was more stable than $CsClBr_2$.

Several of the ammonium trihalides have been prepared. They are very similar to the alkali metal trihalides and are prepared in the same way. Johnson[1] obtained NH_4I_3 by passing ammonia gas into the mother liquor from which the potassium tri-iodide was crystallized. Besides the normal trihalide he also obtained two salts having the composition $NH_4I_3.7KI$ and $5NH_4I_3.KI$ respectively. Roozeboom[2] prepared ammonium tribromide, NH_4Br_3. Chattaway[3] obtained the following trihalides, NH_4Cl_2I, NH_4ClBrI, and NH_4Br_3 and found that the first one was the most stable.

Ray and Sarkar[4] studied the formation of aqueous solutions of $HClI_2$, $HClBr_2$, and $HBrI_2$ by means of the distribution of halogen between an aqueous solution of the acid in question and chloroform, carbon disulfide, or benzene. They found that $HBrI_2$ was the most stable and that the other two were about as stable as the corresponding potassium salts. Cremer and Duncan[5] found evidence for the existence of $HIBr_2$, $HICl_2$, and HIBrCl in solution.

Pentahalides of the Alkali Metals

Wells and Wheeler (loc. cit.) also prepared the following pentahalides: CsI_5, $CsBr_5$, $CsCl.ICl_3$, $RbCl.ICl_3$, $KCl.ICl_3$, $NaCl.ICl_3.2H_2O$, and $LiCl.ICl_3.4H_2O$. The method of preparation is very similar to that used in the preparation of the trihalides. The first five are fairly stable while the last two are very unstable. According to Wells and Wheeler, when the pentahalides are heated they apparently lose halogen and go to the trihalide since the pentahalides all whiten at approximately the same temperature as the corresponding trihalides. On that basis are they listed in Table I.

There are some higher polyhalides described in the literature but there is some doubt about their existence. Abegg and Hamburger found evidence for the existence of KI_7, RbI_7, RbI_9, CsI_7, and CsI_9. Foote and Chalker claimed to obtain KI_7 but none of the other polyiodides with more than five atoms of iodine.

Rae[6] has prepared $CsBr_4$ and $CsBr_3$ and thinks that the tetrabromide was the real compound discovered by Wells and Wheeler and called pentabromide by them. By running the isothermal diagram for the system $CsI - I_2 - H_2O$, Briggs, Greenwald, and Leonard[7] found the CsI_3 and CsI_4 but did not find any evidence for CsI_5.

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[1] Johnson: J. Chem. Soc., **33**, 397 (1878).
[2] Roozeboom: Ber., **14**, 2398 (1881).
[3] Chattaway: J. Chem. Soc., **107**, 105 (1915).
[4] Ray and Sarkar: J. Chem. Soc., **121**, 1449-55 (1922).
[5] Cremer and Duncan: J. Chem. Soc., **133**, 1857-66 (1931).
[6] Rae: J. Chem. Soc., **133**, 1578-81 (1931).
[7] Briggs, Greenwald, and Leonard: J. Phys. Chem., **34**, 1951-60 (1930).

TABLE I

The Alkali Metal Polyhalides

(Arranged in order of increasing stability, based on the temperature at which they whiten when heated in an open tube)

Trihalides		Pentahalides	
Formula	Whiten at Degrees C	Formula	Whiten at Degrees C
$RbClBr_2$	80°	$NaCl.ICl_3.2H_2O$	115°
$RbCl_2Br$	110°	$LiCl.ICl_3.4H_2O$	180°
$RbBr_3$	140°		
$CsClBr_2$	150°		
$CsCl_2Br$	150°		
$CsBr_3$	160°	$CsBr_5$	
KBr_2I	180°		
$RbClBrI$	200°		
KCl_2I	215°	$KCl.ICl_3$	
KI_3	225°		
$CsBrI_2$	260°		
$RbCl_2I$	265°	$RbCl.ICl_3$	
$RbBr_2I$	265°		
RbI_3	270°		
$CsCl_2I$	290°	$CsCl.ICl_3$	
$CsClBrI$	290°		
$CsBr_2I$	320°		
CsI_3	330°	CsI_5	

(The data on the pentahalides are uncertain)

Polyhalides containing Fluorine

At the time these studies were begun no evidence of the existence of polyhalides containing fluorine had been adduced. Cremer and Duncan[1] in studying the dissociation pressures and other properties tried the absorption of iodine bromide by cesium fluoride and found evidence for a compound having the formula $CsFIBr$. It should be very similar in its composition and properties to the cesium chloride-iodine-monobromide. No description or analysis was given and apparently they did not isolate the salt.

Preparation of Fluorine Polyhalides

For the preparation of the fluorine polyhalides four procedures were used. In the first method chlorine was passed into a hot saturated solution of the normal fluoride, containing one equivalent weight of iodine for each atom of fluorine, until all of the iodine color had disappeared. On cooling the solution, small orange-yellow, needle-like crystals were obtained, but these were not all

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[1] Cremer and Duncan: J. Chem. Soc., **133**, 2243-54 (1931).

homogeneous. By careful recrystallization this salt gave a crop of homogeneous crystals. However, this method gave a very poor yield.

The second method tried was practically the same as the first except that the solution of the fluoride was slightly acidified. This gave a much better yield and the crystals were homogeneous when examined under the microscope. In both the above methods of preparation the chlorination was accomplished in an Erlenmeyer flask of appropriate size, fitted with a reflux condenser to return both water and any volatile iodine-chloride formed. The flask was weighed before and after chlorinating and the amount of chlorine absorbed gave some idea as to the compound formed.

In the third or dry method, the normal fluoride was intimately mixed by grinding with one equivalent weight of iodine for each atom of fluorine, and then chlorinated to constant weight in a flask similar to the above with chlorine dried by concentrated sulfuric acid. A dark brown pasty liquid first appeared which gradually changed over to a bright yellow solid. The intermediate product was formed fairly rapidly and probably was a eutectic mixture of iodine monochloride and the fluoride. The final product is formed very slowly. On recrystallizing this solid, very good yields of the same bright yellow, needle-like crystals previously described were obtained. However, this method is too slow.

The fourth and best method found for the preparation of the fluorine polyhalides was to add a slight excess of a cold saturated solution of iodine trichloride to a cold, saturated, slightly acid solution of the normal fluoride. On mixing the two aqueous solutions the characteristic brilliant yellow crystals separated out immediately. After recrystallization, these were entirely homogeneous. A much better yield is obtained by this method than by any of the others.

The iodine trichloride was made by subliming iodine from a glass retort into an ice-cooled flask similar to the other chlorinating flasks while a stream of chlorine in excess of that required to form ICl_3 was sent through it. The bright yellow iodine trichloride deposits on the cold bottom and sides of the flask. This method of forming ICl_3 is much better and quicker than that of chlorinating the solid iodine to the trichloride or to constant weight.

Preparation of the Cesium Fluorine Polyhalide

Cesium chloride was converted to the fluoride by first heating it with an excess of sulfuric acid; this bisulfate was then converted to cesium hydroxide by treating the hot solution of the sulfate with a hot saturated barium hydroxide solution, which precipitated the sulfate as barium sulfate and converted the cesium into cesium hydroxide. By careful addition of the barium hydroxide solution the point was reached at which there was neither sulfate nor barium in solution. The barium sulfate was filtered off and the cesium hydroxide solution was evaporated until the cesium hydroxide or cesium carbonate began to separate. This was then neutralized with hydrofluoric acid. On mixing an aqueous solution of the iodine trichloride with a slightly acid solution of cesium fluoride, the brilliant yellow needles of the cesium polyhalides separated.

The cesium polyhalide is much more stable than the potassium salt, but it does lose halogen slowly in the open. For this reason it is best kept in tightly stoppered bottles. Analyses of this salt (Table II) shows that it has the formula $CsFICl_3$.

TABLE II

Results of Analyses of Salts

Cesium salt, Specimen 1					Theoretical for $CsFICl_3$
Cesium (perchlorate method):	34.27%,			34.33%	34.49% Cs
Cesium salt, Specimen 2					
Cesium (by gentle ignition):	34.59%,			34.56%	
Average (both specimens)				34.44%	34.49% Cs
Chlorine:	27.61%,	28.06%	Average	27.84%	27.62% Cl
Iodine:	33.38%,	32.81%	"	33.09%	32.96% I
				95.37	
Fluorine by difference:				4.63%	4.93% F
Rubidium salt					Theoretical for $RbFICl_3$
Rubidium:	25.27%,	25.43%	Average	25.35	25.30% Rb
Chlorine:	31.46%,	31.52%	"	31.49	31.50% Cl
Iodine:	37.52%,	38.05%	"	37.78	37.58% I
				94.62	
Fluorine by difference				5.38	5.62% F
Potassium salt					Theoretical for $KFICl_3$
Potassium:	13.37%,	13.31%	Average	13.34	13.42% K
Chlorine:	36.60%,	36.46%	"	36.53	36.51% Cl
Iodine:	43.57%,	43.67%	"	43.62	43.75% I
				93.49	
Fluorine by difference				6.51	6.32% F
Ammonium salt					Theoretical for NH_4FICl_3
NH_3 calc. to NH_4F:	13.57%,	13.53%	Average	13.55%	13.68%
Chlorine:	39.39%,	39.32%	"	39.36%	39.44% Cl
Iodine:	46.79%,	46.82%	"	46.81%	46.90% I
				99.72%	

Preparation of the Rubidium Fluorine Polyhalide

Starting with rubidium chloride, the rubidium fluorine polyhalide was prepared in the same way as the cesium salt. The rubidium fluorine polyhalide is similar to the cesium salt. It is much more stable than the corresponding potassium salt but not quite as stable as the cesium salt. Analyses (Table II) show it has the formula $RbFICl_3$.

Preparation of the Potassium Fluorine Polyhalide

The potassium fluoride used was obtained from the pure acid fluoride either by fusing and driving off hydrogen fluoride leaving the normal fluoride, or by neutralizing the acid fluoride in solution with potassium carbonate. The polyhalides of potassium were prepared by all four methods described above although method 4 was best. The salt is so unstable that at first no consistent analyses could be obtained. However, it was found that the loss of halogen occurred during separation of the crystals from the mother liquor and drying. This was obviated by collecting the crystals in a covered Jena fritted glass Gooch crucible and immediately centrifuging at high speed still keeping the potassium salt covered in the crucible. The salt was immediately transferred to tiny weighing bottles which were almost completely filled by the sample (to avoid loss of ICl_3). Excellent analyses, establishing the formula as $KFICl_3$, were obtained in this fashion as shown in Table II.

Preparation of the Ammonium Fluorine Polyhalide

Pure ammonium bifluoride was almost completely neutralized with ammonia and to this cold solution a cold saturated solution of iodine trichloride was added. The yellow crystals were collected and separated from mother liquor centrifugally as in the case of the potassium salt. The analyses (Table II) showed the salt to have the formula NH_4FICl_3.

Trihalides containing Fluorine

In addition to the fluorine pentahalides, an attempt was made to prepare the fluorine trihalides of the alkali metals by mixing a solution of the fluoride with a solution of iodine monochloride, by treating the solid fluoride with liquid iodine monochloride, and by chlorinating a suspension of iodine in an aqueous solution of the fluoride, both hot and cold. If any compound was formed it was too unstable to be isolated.

Methods of Analysis

On all the salts a complete analysis was made, save for fluorine which was determined by difference. In the first cesium fluorine polyhalide specimen prepared the cesium was determined as cesium perchlorate and in the second as cesium fluoride. It was found that the same or better results could be obtained by the latter method of gently igniting the polyhalide, whereupon all the cesium was left as cesium fluoride. This latter method was also used on the rubidium and potassium salt. In no case did the residue after ignition contain even a trace of chlorine or iodine.

The chlorine and iodine were determined by the method of Gooch. In this method two sets of samples are run, one in which the chlorine and iodine are both precipitated as the silver salts, and in the other set only the chlorine is precipitated as the silver salt. In both cases the samples were gently heated with dilute ammonium hydroxide solution to convert the chlorine and iodine into the chloride and iodide. The first set of samples were then acidified while the second were treated with dilute sulfuric acid and potassium nitrite to expel the iodine. The solution was boiled gently until the disappearance of the iodine color. The silver halides were precipitated and the chlorine determined in the usual way. If equal weight samples are used in both cases, the difference in weight in the silver salts represents the weight of silver iodide in the former case. This method is not quite as satisfactory as might be desired, due to the fact that there is danger both of not expelling all of the iodine and also of driving off some of the chlorine. The ammonium salt was analyzed for NH_3 by distilling with excess alkali, absorbing in standard acid and back-titrating; and the NH_3 was reported as NH_4F.

Properties

The cesium, rubidium, potassium, and ammonium fluorine-iodine-trichlorides have very much the same physical properties; they all have the same orange yellow color, crystalline form, and general properties but differ in their stability and the temperature at which they decompose. When the normal fluoride solution is mixed with the solution of iodine trichloride, the pentahalide separates out as brilliant, orange-yellow, needle-like, tetragonal prisms exhibiting parallel extinction under crossed nicols in two positions and isotropic in the third.

The cesium salt is the most stable. When heated in an open tube it melts and then decomposes well above 300°C.; although there is a slight decomposition below that temperature. When heated in a sealed tube it melts at 194° but on cooling there seems to have been no decomposition. The specific gravity of the $CsFICl_3$ is 3.565.

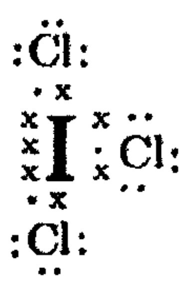
The rubidium salt is much more stable than the corresponding potassium salt but is not quite as stable as the cesium salt. When heated in an open tube the rubidium pentahalide melts and decomposes at approximately 300°. When heated in a closed tube, $RbFICl_3$ melts without decomposition at 172°.

The specific gravity of the rubidium polyhalide is 3.159. The potassium salt is the least stable.

When the mother liquor from which the alkali metal fluorine polyhalide is precipitated is evaporated to dryness there is very little residue left. This shows that the fluorine pentahalides are not very soluble in water. The polyhalides are not soluble in and do not react with carbon tetrachloride and are insoluble in benzene but react with it if allowed to stand in contact with it for a long period of time.

Structure

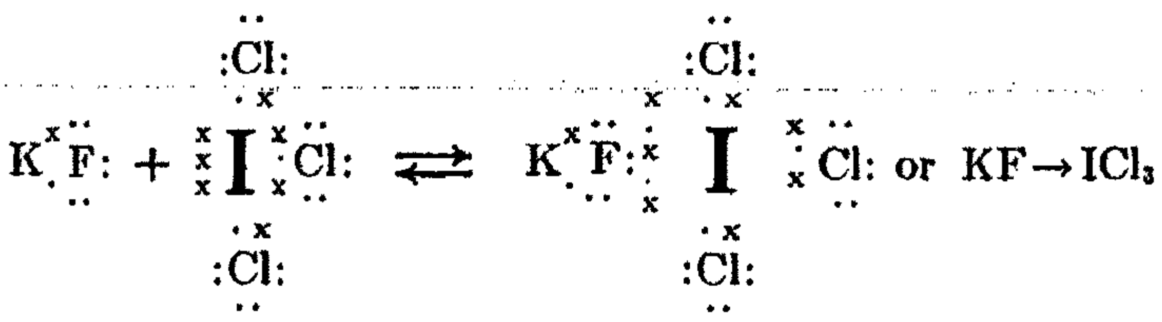
The structure of ICl_3 may be represented by



$$\begin{array}{cl} :\ddot{\mathrm{Cl}}: & \\ \cdot\times & \\ \overset{\times}{\underset{\times}{\mathrm{I}}}\ \ \overset{\times}{\underset{\times}{}}\!: & \!\!\mathrm{Cl}: \\ \cdot\times & \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: & \end{array}$$

in which the central I atom has ten electrons. However, according to Sidgwick, a decet is not a particularly stable arrangement, and it is not surprising that ICl_3 tends to combine with the alkali fluorides to form pentahalides.

In this process the fluorine probably acts as a donor and the iodine as an acceptor increasing the electronic environment of the iodine to the more stable duo-decet, as follows:



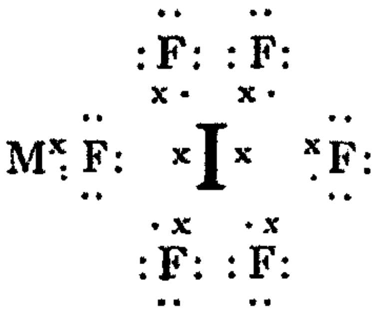
$$\mathrm{K}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: + \begin{array}{c} :\ddot{\mathrm{Cl}}: \\ \cdot\times \\ \overset{\times}{\underset{\times}{\times}}\mathrm{I}\overset{\times}{\underset{\times}{}}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \\ \cdot\times \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array} \rightleftarrows \mathrm{K}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\overset{\times}{:}\ \begin{array}{c} :\ddot{\mathrm{Cl}}: \\ \cdot\times \\ \mathrm{I} \\ \cdot\times \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array}\ \overset{\times}{\underset{\times}{\cdot}}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \text{ or } \mathrm{KF}\rightarrow\mathrm{ICl_3}$$

The great stability of the duo-decet is revealed in such a compound as SF_6. As would be expected, the most stable polyhalide is formed with the alkali of highest atomic number, where the greater distance of the valence electrons from the nucleus facilitates the donation of two of the fluorine electrons.

Undoubtedly fluorine polyhalides of this same type with other metallic elements could be prepared by similar methods. Thermal analysis of the system HF-ICl_3 may also reveal new compounds.

Of this same type would be compounds formed by the union of BrF_3 with MX, yielding $MFBrF_3$, $MClBrF_3$, etc.

Iodine pentafluoride should combine with alkali halides to form $KXIF_5$ in which two of the electrons of the iodine atom would be inert as in



$$\begin{array}{ccc} & :\ddot{\mathrm{F}}:\ :\ddot{\mathrm{F}}: & \\ & \times\cdot\quad\times\cdot & \\ \mathrm{M}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: & \times\mathrm{I}\times & \overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: \\ & \cdot\times\quad\cdot\times & \\ & :\underset{\cdot\cdot}{\mathrm{F}}:\ :\underset{\cdot\cdot}{\mathrm{F}}: & \end{array}$$

Even iodine heptafluoride might combine to yield compounds of the type $MXIF_8$, since the stable shell of sixteen electrons is known in such a compound as OsF_8.

Investigation of these predicted compounds is now well under way in this laboratory, and will be reported shortly.

Summary

It was found that the most satisfactory method of preparing the fluorine polyhalides of the type formula $MFICl_3$ was to mix a saturated solution of the alkali fluoride with a saturated solution of iodine trichloride, both solutions being cold at the time of mixing.

The cesium and rubidium salts are both fairly stable, the ammonium salt less, and the potassium least, though over a long period of time the cesium and rubidium salt lose halogen unless kept in tightly stoppered bottles or in a desiccator containing a few crystals of iodine trichloride.

The fluorine polyhalides are insoluble in benzene and carbon tetrachloride but react with the former slowly. The solubility in water is limited but is greater with the ammonium and potassium salts.

The four polyhalides prepared form orange-yellow tetragonal crystals exhibiting parallel extinction.

It is established that fluorine can form part of a polyhalide.

Cleveland, Ohio.

STUDIES ON HYDRAZINE: SOLUBILITY OF HYDRAZINIUM SALTS IN MIXED SOLVENTS*

BY E. C. GILBERT AND E. H. HUFFMAN

The solubility of electrolytes in mixed solvents has been the subject of many investigations[1] but the problem is of such complexity that additional work is much to be desired. Many of the salts of hydrazine are soluble both in alcohols and in water and it was hoped that they might prove a suitable medium for an investigation over the entire field. The picrate and trinitro-m-cresylate were chosen particularly because their solubility, while sufficient for easy determination, is not so large as to require large amounts of material, and their solubility in water and alcohol are of the same order. They are both salts containing one equivalent of hydrazine to one of acid and are hydrated. The solubility of hydrated salts in mixtures of alcohol and water presents a special phase of the general problem and has been studied by Bödtker[2] and by D'Ans and Siegler.[3]

The solubility of picric acid in alcohol and water mixtures has also been studied.[4] Duff and Bills found a maximum solubility in mixtures of ethyl alcohol and water containing 80% alcohol by weight. Their results differed from those of Angelescu and Dumitrescu and it was hoped that a study of the salts of the acid might show whether the increased solubility is due to the picrate ion or to the acid.

Experimental

Materials: Hydrazinium picrate and trinitro-m-cresylate were prepared by reaction of the base and acid in alcohol and recrystallized from water three times. This procedure leaves the picrate with one-half molecule of water and the cresylate with one molecule.

Analysis: Hydrazinium picrate; $N_2H_5^+$ found, 12.19, 12.12, 12.23 percent. Calc. for $N_2H_5OC_6H_2(NO_3)_3.\frac{1}{2}H_2O$, 12.23%.

Hydrazinium trinitro-m-cresylate; $N_2H_5^+$ found, 11.31, 11.25, 11.31, 11.27 percent. Calc. for $N_2H_5OC_6H(NO_3)_3CH_3.H_2O$, 11.28%.

When dried over concentrated sulfuric acid the cresylate loses its water but the picrate does not.[1] The anhydrous cresylate melts at 172-173° with decomposition.

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* Contribution from the Department of Chemistry, Oregon State College.

[1] Lobry de Bruyn: Z. physik. Chem., **10**, 782 (1892); Bödtker: **22**, 505 (1897); Herz and Anders: Z. anorg. Chem., **52**, 164 (1907); **55**, 271 (1907); Herz and Knoch: **41**, 351 (1904); **45**, 262 (1905); Herz and Kuhn: **58**, 159 (1908); **60**, 152 (1908); Wright: J. Chem. Soc., **121**, 225 (1922); Treadwell: Helv. Chim. Acta, **4**, 982 (1921); Angelescu and Dumitrescu: Z. physik. Chem., **132**, 217 (1928); Gregg-Wilson and Wright: J. Chem. Soc., **1928**, 3111; Duff and Bills: **1931**, 1196; and others.

[2] Bödtker: Loc. cit.

[3] D'Ans and Siegler: Z. physik. Chem., **82**, 35 (1912).

[4] Duff and Bills: Loc. cit; Angelescu and Dumitrescu: Loc. cit.

Commercial absolute ethyl alcohol was treated with sodium and distilled. The first and last portions were discarded. The middle portion boiling over a range of 0.02° proved to be 99.8 percent alcohol by volume and gave negative tests for aldehydes. The water was of conductivity grade.

Procedure: Mixtures of alcohol and water were made by weight and samples of the salt rotated with the solvent to constant solubility at 20° ±0.01. Samples were withdrawn with a pipette and the hydrazine determined by the iodic acid method.[2] The titration is carried out in acid solution and repeated tests showed the alcohol to be without effect on the titration.

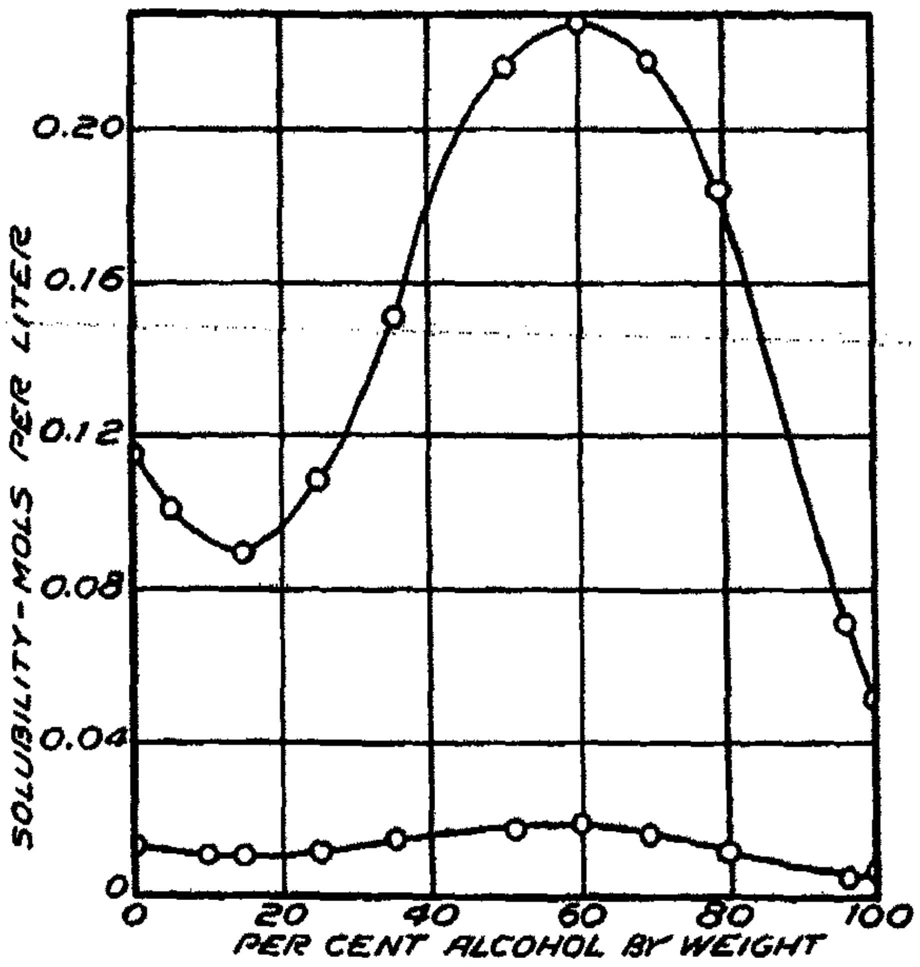

Fig. 1

Solubility of Hydrazinium Salts in Alcohol-Water Mixtures at 20. Upper curve—Cresylate; Lower curve—Picrate

The solubility relations of the cresylate not having been previously published, the solubility curve in pure water from 15° to 30° was also determined by the same procedure.

Results and Discussion

The results are shown in Tables I and II and in Fig. 1. Both salts show very interesting solubility curves containing maxima and minima which however seem to be of doubtful value for the purpose of studying general solvent action. Due to the fact that both are plotted on the same scale the curve for the cresylate seems to have a more abrupt slope but the percentage increase or decrease in solubility is nearly the same for both salts. It is evident

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[1] Gilbert: J. Am. Chem. Soc., 53, 3957 (1931).

[2] Bray and Cuy: J. Am. Chem. Soc., 46, 858 (1924).

TABLE I

Solubility of Hydrazinium Picrate and Trinitro-*m*-cresylate in Ethyl Alcohol—Water Mixtures at 20°

Percent Alcohol by weight	Solubility	Mols/Liter
	Picrate	Cresylate
0.00	0.01396	0.1158
5.00		0.1015
10.00	0.01160	
15.00	0.01076*	0.08996
25.00	0.01113	0.1089
34.50	0.01448*	0.1509
50.00		0.2170
51.00	0.01890	
60.00	0.01901	0.2297
69.40	0.01616	0.2189
79.70	0.01176	0.1843
96.00	0.00525	0.0710
99.8**	0.00694	0.0517

* Result of one determination
** By volume

TABLE II

Solubility of Hydrazinium Trinitro-m-cresylate in Water

Temperature	Solubility Mols/Liter
15.0	0.08473
20.0	0.1158
25.0	0.1506
30.0	0.2053

that compounds, either hydrates or alcoholates, are formed in solution. These compounds are not stable in the dry state for the solid residue was removed from solutions containing 5, 60, 80, 96, and 99.8 percent alcohol, dried by washing with anhydrous ether, and in every case proved upon analysis to be the original compound. The water of hydration was retained even in 99.8 percent alcohol, but no evidence of an alcoholate was ever detected. Lobry de Bruyn[1] found certain hydrated salts which retain water even in pure alcohol, but D'Ans and Siegler[2] found with $Ca(NO_3)_2$ evidence of a definite alcoholate. The solubility curve in this case showed definite cusps and breaks in continuity in contrast with the smooth curves found in the present work.

The curves for the two salts show no resemblance to that of the free picric acid, perhaps due to the water of hydration, but show a general resemblance to the results of Angelescu and Dumitrescu[1] for the solubility of picric acid in certain mixed organic solvents.

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[1] Lobry de Bruyn: Loc. cit.
[2] D'Ans and Siegler: Loc. cit.
[3] Angelescu and Dumitrescu: Loc. cit.

The point of maximum solubility for the salts lies in solutions of lower alcohol content than that for the free acid.[1]

When solubility determinations were attempted with the anhydrous salts, they took water even from 96 percent alcohol and only when completely hydrated were concordant results obtained for the solubilities. The solubility of the picrate agrees well with earlier work[2] (in water). It is interesting to note that contrary to reasonable prediction, the insertion of a CH_3 group into the picrate to form the cresylate increases the solubility in water ten-fold, rather than decreasing it.

Summary

1. The solubility of hydrazinium picrate and trinitro-m-cresylate have been determined in ethyl alcohol-water mixtures at 20°.

2. Both salts give a peculiar solubility curve with maxima and minima, but no evidence was found of the formation of a stable alcoholate.

3. These salts retain their water of hydration even in 99.8% alcohol, and the anhydrous salts take up water from aqueous alcohol.

4. The solubility curve for the salts shows no resemblance to that of the free acid in the same solvents.

5. The solubility of hydrazinium trinitro-m-cresylate has been determined in water over a range of temperatures.

Corvallis, Oregon.
July 7, 1932.

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[1] Duff and Bills: Loc. cit.

[2] Gilbert: J. Phys. Chem., 33, 1235 (1929).

DENSITIES OF SATURATED VAPOURS

BY ROBERT WRIGHT

The densities of saturated vapours have been less frequently determined than those of unsaturated. In the method here described the experimental detail is simple but the temperature of the determination is confined to that of the boiling point of the liquid yielding the vapour.

A small quantity of the liquid to be investigated is placed in a previously weighed stoppered cylindrical bulb of about 100 cc capacity. The bulb is bound by means of twine between two curved brass strips, which are soldered to two stout brass wires about 80 cm. long, care being taken that there is no direct metallic contact between the two supports. The strips should extend slightly below the bottom of the bulb, and the wires, which are soldered along the backs of the strips, should project about 1 cm beyond their lower ends. The ends of the wires below the bulb are joined by a spiral of fine platinum wire arched upwards so as to touch the bottom of the glass bulb. The upper ends of the wires pass through a cork carrying a short condenser, and the bulb and its support are suspended in the outer jacket of an ordinary Victor Meyer vapour density apparatus, in which is placed 50 – 100 cc of the liquid under investigation.

In carrying out an investigation the liquid in the jacket is boiled so that its vapour rises well above the top of the suspended bulb, which is unstoppered during the heating. The brass supporting wires are now connected to a low voltage battery and a suitable current passed through the heating spiral under the bulb. This current should be of such strength that it will evaporate the liquid in the bulb in about 15 minutes. After evaporation is complete the vapour in the bulb is at a temperature somewhat higher than its boiling point, the current is now stopped and the apparatus left for about 10 minutes till the temperature of the bulb falls to that of the surrounding boiling vapour. The bulb is now filled with saturated vapour, it is removed from the heating jacket and immediately stoppered.

After cooling to room temperature the stopper is loosened to admit air, and the bulb is weighed. Even neglecting the small volume occupied by the condensed vapour the bulb now contains less air than at its first weighing, since air is prevented from entering owing to the vapour pressure of the liquid in the bulb. The total pressure in the bulb is the barometric pressure B, and if the pressure due to the vapour is P, then the volume of air replaced by vapour $= \frac{P}{B}V$, where V is the volume of the bulb. This volume, multiplied by the weight of 1 cc of air gives the weight of air excluded from the bulb by the vapour, and this weight must be added to that obtained at the second weighing, in order that the difference between the first and second weighings should correspond to the weight of the vapour.

The vapour pressure of the liquid at the temperature of the weighing may either be obtained from tables or else determined directly by the following simple method.

The closed end of a barometer tube is expanded into a bulb and then bent so as to lie parallel with the rest of the tube. A small quantity of the liquid under investigation is introduced into the bulb, and the open end of the tube is then fitted by means of a rubber stopper into a filter flask containing a layer of mercury. On exhausting the flask by a water pump, and slightly heating the bulb, all the air can be driven out of the barometer tube by means of the vapour stream. After disconnecting the pump, mercury rises in the tube, and allowing the apparatus to cool the vapour pressure may be read directly.

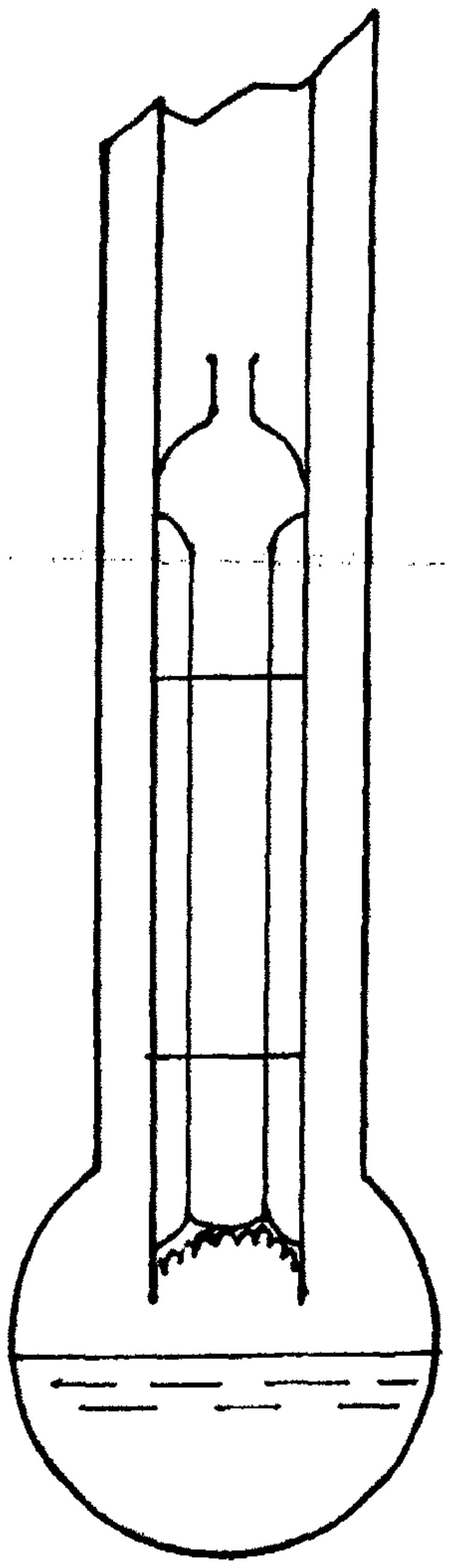

FIG. 1

From the weight of the condensed vapour and the volume of the flask the density of the saturated vapour can be calculated. In the table are given the saturated vapour densities (grams per cc.) of a number of simple organic compounds at their boiling points, and the corresponding molecular weights calculated from the relative densities are also given. It will be seen that the molecular weights are close to the normal values except in the case of acetic acid, which is known to be associated to a considerable extent in the gaseous state. In the case of acetic acid the supporting wires were made of silver as brass is readily attacked by the vapour of the boiling acid.

The existence of a minimum in the vapour pressure curve of a binary liquid mixture is frequently assumed to indicate complex formation between the two constituents of the mixture. Such a minimum is shown by the system chloroform-acetone, and it is of interest to determine whether the vapour of such a system shows any indication of the existence of a compound in the gaseous state.

For this purpose the saturated vapour density of the constant boiling mixture was determined, it being considered that the formation of complex molecules would be more probable in saturated than in unsaturated vapour.

The experimental values found for the vapour density relative to hydrogen in two determinations were 48 and 48.3, corresponding to molecular weights of 96 and 96.6. The refractive index of the mixture was 1.41318 corresponding to 22% acetone and 78% chloroform, or 36.5 Mol % acetone and 63.5 Mol % chloroform. On the assumption that there is no union between the molecules of the vapours, the composition corresponds to a molecular weight of 96.7, a value practically identical with the experimental figure. The results given in Table I therefore indicate that in the state of vapour there is no union between the molecules of acetone and chloroform.

TABLE I

	B. Pt.	M. Wt. (found)	M. Wt. (Cal.)	Density at 760 mm.
Alcohol	78°	46.4	46	.00162
		46.8		.00164
Benzene	80°	80.0	78	.00275
		79.6		.00274
Toluene	110°	96.0	92	.00302
		94.6		.00298
Chloroform	60°	119.0	119	.00437
		118.0		.00433
Carbon tetra-chloride	75°	158.0	154	.00452
		157.0		.00550
Acetone	56°	57.8	58	.00213
		57.4		.00211
Acetic acid	118°	100.2	60	.00314
		102.0		.00318

Physical Chemistry Department,
Glasgow University.
July 1, 1932.

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES

IV. Arsenic Trisulfide Sol

BY HARRY B. WEISER AND GEORGE R. GRAY

In earlier papers, the displacement of chloride ions from colloidal particles by the stepwise addition of electrolytes to the positive hydrous oxide sols of iron, chromium, and aluminum, has been followed potentiometrically and the adsorption isotherms for the precipitating ions have been determined.[1] These observations have led to a proposed mechanism of the electrolyte coagulation process. The present paper deals with similar potentiometric titration and adsorption studies on negative As_2S_3 sol. This type of investigation on As_2S_3 sol should prove fruitful since Whitney and Ober,[2] in their classical observations on adsorption during the coagulation of this sol, pointed out that the adsorption of cations was accompanied by the setting free of an equivalent amount of acid.

Historical

Following Linder and Picton's[3] observations that barium but not chlorine is carried down during the coagulation of As_2S_3 sol by $BaCl_2$, Whitney and Ober investigated quantitatively the adsorption of barium, strontium, calcium, and potassium during coagulation by the respective chlorides. As a result of these studies it was concluded that equivalent amounts of the respective cations were carried down during the coagulation process. The filtrate from the coagulum contained free acid which was found by titration with alkali to be equivalent in quantity to the cation adsorbed. The phenomenon was believed by both Linder and Picton, and Whitney and Ober to be a case of hydrolytic adsorption in which equivalent amounts of cation and hydroxyl were carried down with the precipitate leaving HCl in solution. Rabinowitsch[4] showed, however, that the adsorption does not cause hydrolytic cleavage of the salt. For example, the adsorption of barium was determined (1) from the difference in concentration of $Ba^{\cdot\cdot}$ ion before and after coagulation; (2) from the difference in weight of the dry As_2S_3 precipitate after coagulation with $BaCl_2$ and HNO_3, respectively. The adsorption values by the two methods agreed quite well, showing that the barium was not carried down as $Ba(OH)_2$. Moreover, the precipitate was free from chloride. The process would, therefore, appear to involve exchange adsorption in which hydrogen ions on the particles are exchanged for barium ions.

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[1] Weiser: J. Phys. Chem., **35**, 1, 1368 (1931); Weiser and Gray: **36**, 2178 (1932).

[2] J. Am. Chem. Soc., **23**, 842 (1901).

[3] J. Chem. Soc., **67**, 63 (1895).

[4] Z. physik. Chem., **116**, 97 (1925).

Contrary to the belief of Whitney and Ober and of Freundlich,[1] Weiser[2] pointed out that the amounts of several cations carried down during the coagulation of As_2S_3 sol are not necessarily equivalent. Moreover, the amount of adsorption of a given cation varies widely with different sols, depending as it does on the method of preparation, age, and concentration of the sol.

Since the platinum and quinhydrone electrodes can not be used successfully with As_2S_3 sol, Pauli and Semler[3] used conductometric methods to determine the $H^{\cdot}$ ion concentration of a dialyzed sol and of the filtrate after coagulation of the sol by electrolytes. They found the ratio between $[H^{\cdot}]$ in the filtrate and adsorbed $\frac{1}{2}$ $[Ba^{\cdot\cdot}]$ ion to be 4 : 1 instead of 1 : 1 as reported by Whitney and Ober. Pauli and Semler considered the sol to be a strongly dissociated complex acid to which they assigned the formula $(xAs_2S_3 \cdot As_2S_4H_2 \cdot As_2S_4H)' + H^{\cdot}$. This formula was made to fit the specific case where but one of four $H^{\cdot}$ ions are displaced by $Ba^{\cdot\cdot}$, the remaining three appearing in solution only after coagulation.

Rabinowitsch[4] likewise determined the $H^{\cdot}$ ion concentration of As_2S_3 sol before and after coagulation using conductometric methods. He found the total $H^{\cdot}$ ion concentration of the filtrate after coagulation to be equal to the $Ba^{\cdot\cdot}/2$ adsorbed, confirming the earlier observations of Whitney and Ober. The sol was therefore assigned the general formula $[(As_2S_3)_xSH]' + H^{\cdot}$, first suggested by Linder and Picton.

Since the ratios of $H^{\cdot}$ ion in the filtrate to $Ba^{\cdot\cdot}$ adsorbed with different sols have been found to be 1 and 4, using similar methods of analysis, it is altogether probable that an indefinite number of different ratios could be obtained by suitable modifications in the method of preparing the sol. The formulas of Pauli and Semler and of Rabinowitsch are, therefore, without any general significance. Rabinowitsch points out that he used an undialyzed sol while Pauli and Semler used one that had been dialyzed. To the extent that dialysis influences the ratio under consideration, it is obvious that one can get considerable variation with the same preparation simply by varying the method and time of dialysis.

The conductometric method of determining the $H^{\cdot}$ ion concentration in sol-electrolyte mixtures is of doubtful accuracy, at least in certain cases. Rabinowitsch[5] first used a graphic method to evaluate the $H^{\cdot}$ ion concentration from conductometric data but the results did not agree with glass-electrode measurements.[6] Fairly good agreement was obtained if the concentration C was calculated from the expression $C = \frac{1000\, X_{ac}}{u_H + u_c}$, where u_H and u_c are the mobilities of $H^{\cdot}$ and the added cation, respectively, and

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[1] Kolloid-Z., 1, 32 (1907).

[2] J. Phys. Chem., 29, 955 (1925).

[3] Kolloid-Z., 34, 145 (1924).

[4] Z. physik. Chem., 116, 97 (1925).

[5] Z. physik. Chem., 116, 97 (1925); Rabinowitsch and Dorfmann: 131, 313 (1928).

[6] Rabinowitsch and Kargan: Z. physik. Chem., 143, 21 (1929).

$x_{ac} = x - x_o - L\frac{\Delta x_g}{\Delta L}$, x and x_o being the conductivity before and after the addition of electrolyte, L, the number of cc of electrolyte added, and $\Delta x_g/\Delta L$, the change in conductivity with change in the amount of electrolyte added after the conductivity curve assumes a straight course. For salts with univalent cations $L\frac{\Delta x_g}{\Delta L}$ has to be replaced by Δx from Kohlrausch's law, in order to get results which agree at all well with glass electrode measurements. These formulas fail to take into account both the change in activity of the added salt in the sol and the mobility of the colloidal particles. Since both of these have an effect, the method can, at best, yield only approximately accurate results. Fortunately, there is no apparent need of using a conductometric method to follow the change in hydrogen ion concentration. The glass electrode has been found satisfactory in many cases where the platinum and quinhydrone electrodes are not suitable and it would seem to be well adapted to the case at hand. Rabinowitsch and Kargan used it in three experiments to determine the change in hydrogen ion concentration during the coagulation of As_2S_3 sol, with KCl, $BaCl_2$ and $AlCl_3$, respectively; but unfortunately their data cannot be compared. The implication is that they used the same sol for all three cases but, if they did, there was something radically wrong with their procedure as the difference in pH of the original samples used with KCl and $BaCl_2$ was almost as great as the total change in pH on adding the electrolyte. In the subsequent experiments it will be shown that the glass electrode gives consistent, reproducible results with As_2S_3 sol-electrolyte mixtures.

Experimental

A. *General Method of Procedure.*

Preparation of Sols. The As_2S_3 sols were prepared according to the procedure of Freundlich and Nathansohn.[1] Saturated As_2O_3 solution was diluted with a solution containing 1 cc of saturated H_2S solution per 100 cc. After the appearance of a light-yellow coloration, a solution of H_2S ten times as strong as the above was added. The solution was then saturated with H_2S gas and the excess washed out with H_2. After standing overnight, the sol was filtered and the titrations were carried out. The sol was protected at all times from the action of light. All the experiments on a given sol were completed within a few days to avoid changes brought about by ageing.

Method of Titration. To 10 cc of As_2S_3 sol contained in a weighing bottle were added varying amounts of water and precipitating electrolyte, bringing the final volume to 15 cc. A definite procedure of mixing was followed in each case. Preliminary experiments with dilute sols using 0.004 N $CaSO_4$ as coagulating electrolyte showed a decrease in pH for small amounts added, followed by an increase in pH at higher concentrations of electrolyte. This effect was found to be due to the slight alkalinity of the electrolyte (probably a trace of $Ca(OH)_2$). In all of the experiments herein recorded, the pH of the sol was first determined and then the pH of the water and of the electrolyte

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[1] Kolloid-Z., **28**, 258 (1921).

were brought to this value by the addition of H_2SO_4 in the case of $CaSO_4$ and of HCl with the several chlorides. Thus the observed displacement of $H^\cdot$ ions was real, being due to the added cations and not to dilution effects. After the mixtures were made up, they were stoppered and allowed to stand in the dark for 18 hours before making the potentiometric measurements.

Potentiometric Measurements. The glass electrode was employed in the determination of $H^\cdot$ ion concentration. A bulb was blown on the end of a piece of glass tubing of suitable composition.[1] The bulb was filled with 1 *N* HCl and allowed to stand in distilled water for several days before using.

In making the e.m.f. measurements a vacuum tube potentiometer constructed by Mr. M. F. Roy according to the specifications of Stadie[2] was employed in conjunction with a type K Leeds and Northrup potentiometer and a Hartman and Braun moving-coil galvanometer.

The glass bulb containing 1 *N* HCl was suspended in the weighing bottle containing the sol-electrolyte mixture. The tip of the salt bridge from the saturated calomel electrode making contact with the HCl, was drawn out to a fine point and plugged with cotton. To minimize the coagulation of the sol by the saturated KCl, a piece of glass tubing 3 cm long having one end covered with cellophane and containing distilled water, was attached to the tip of the bridge arm making contact with the liquid in the weighing bottle. This tube was removed and flushed out after each measurement.

To calculate the pH from the e.m.f. measurements the glass electrode was standardized with *M*/20 potassium acid phthalate, which has a pH of 3.97.[3] The solution was placed in a weighing bottle and all contacts were made in the manner outlined above. The pH of the sol-electrolyte mixture is given by the formula: $\text{pH of mixture} = 3.97 \pm \dfrac{\text{e.m.f. of phthalate} - \text{e.m.f. of mixture}}{0.0001984T}$. In subsequent tables the e.m.f. of the potassium acid phthalate solution is designated "E_0". This method of standardization eliminates errors due to inequalities between the calomel electrodes and to liquid-liquid contact potentials. Other standard buffers of lower pH were frequently run as controls.

B. Variation in Hydrogen Displacement with Concentration of Sol.

Sols of different concentrations were investigated to find a satisfactory one for simultaneous measurements of hydrogen displacement and cation adsorption. It would be expected that with sols prepared under similar conditions, the most concentrated sol would show the greatest hydrogen ion displacement. This view was confirmed by the following experiment: As_2S_3 sols I, II, and III, containing 1.70, 4.38, and 10.80 g/l, respectively, were titrated with 0.004 *N* $CaSO_4$. Most of the data are recorded in Table I, but to conserve space a portion of the observations are omitted after the pH value attained a constant value. All of the $H^\cdot$ ion displacement data are shown graphically in Fig. 1.

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[1] McInnes and Dole: J. Am. Chem. Soc., **52**, 29 (1930). Glass used was from Corning Glass Co., their No. 015.

[2] J. Biol. Chem., **83**, 477 (1929).

[3] Clark and Lubs: J. Biol. Chem., **25**, 506 (1916); Clark: "The Determination of Hydrogen Ions," 3rd. ed. 485 (1928).

TABLE I

Titration of As_2S_3 Sols with 0.004 *N* $CaSO_4$

(10 cc of sol. Total volume 15 cc. 30°C)

Cc of 0.004 *N* $CaSO_4$ added	π milli-volts	pH	[H] × 10^5 in solution	[H] × 10^5 displaced	½ [Ca] × 10^5 added
		Sol I 1.70 g/l	E_o = 169.6 mv		
0.0	170.2	3.98	10.5	0.0	0.0
0.5	164.1	3.88	13.2	2.7	13.3
1.0	164.3	3.88	13.2	2.7	26.7
1.5	163.6	3.87	13.5	3.0	40.0
2.0	164.9	3.89	12.9	2.4	53.3
2.5	163.9	3.88	13.2	2.7	66.7
3.0	164.1	3.88	13.2	2.7	80.0
5.0	164.2	3.88	13.2	2.7	133.3
		Sol II 4.38 g/l	E_o = 182.5 mv		
0.0	154.9	3.51	30.9	0.0	0.0
0.5	151.5	3.45	35.5	4.6	13.3
1.0	149.5	3.42	38.0	7.1	26.7
1.5	150.1	3.43	37.2	6.3	40.0
2.0	149.7	3.42	38.0	7.1	53.3
2.5	148.9	3.41	38.9	8.0	66.7
3.0	149.2	3.42	38.0	7.1	80.0
5.0	149.0	3.41	38.9	8.0	133.3
		Sol III 10.80 g/l	E_o = 165.4 mv		
0.0	125.4	3.30	50.1	0.0	0.0
0.5	119.7	3.21	61.7	11.6	13.3
1.0	118.1	3.18	66.1	16.0	26.7
1.5	116.9	3.16	69.2	19.1	40.0
2.0	116.2	3.15	70.8	20.7	53.3
2.5	115.9	3.14	72.5	22.4	66.7
3.0	115.4	3.14	72.5	22.4	80.0
5.0	115.5	3.14	72.5	22.4	133.3

The displacement follows a smooth course similar to the usual adsorption isotherm. It is of interest to note that the maximum displacement of hydrogen ions occurs before the precipitation concentration (approximate value indicated by a vertical line cutting the curve) is reached. A similar behavior was reported with $BaCl_2$ by Rabinowitsch and Fodimann,[1] who confirmed Briggs'[2]

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[1] Z. physik. Chem., 154 A, 255 (1931).

[2] J. Phys. Chem., 34, 1326 (1930).

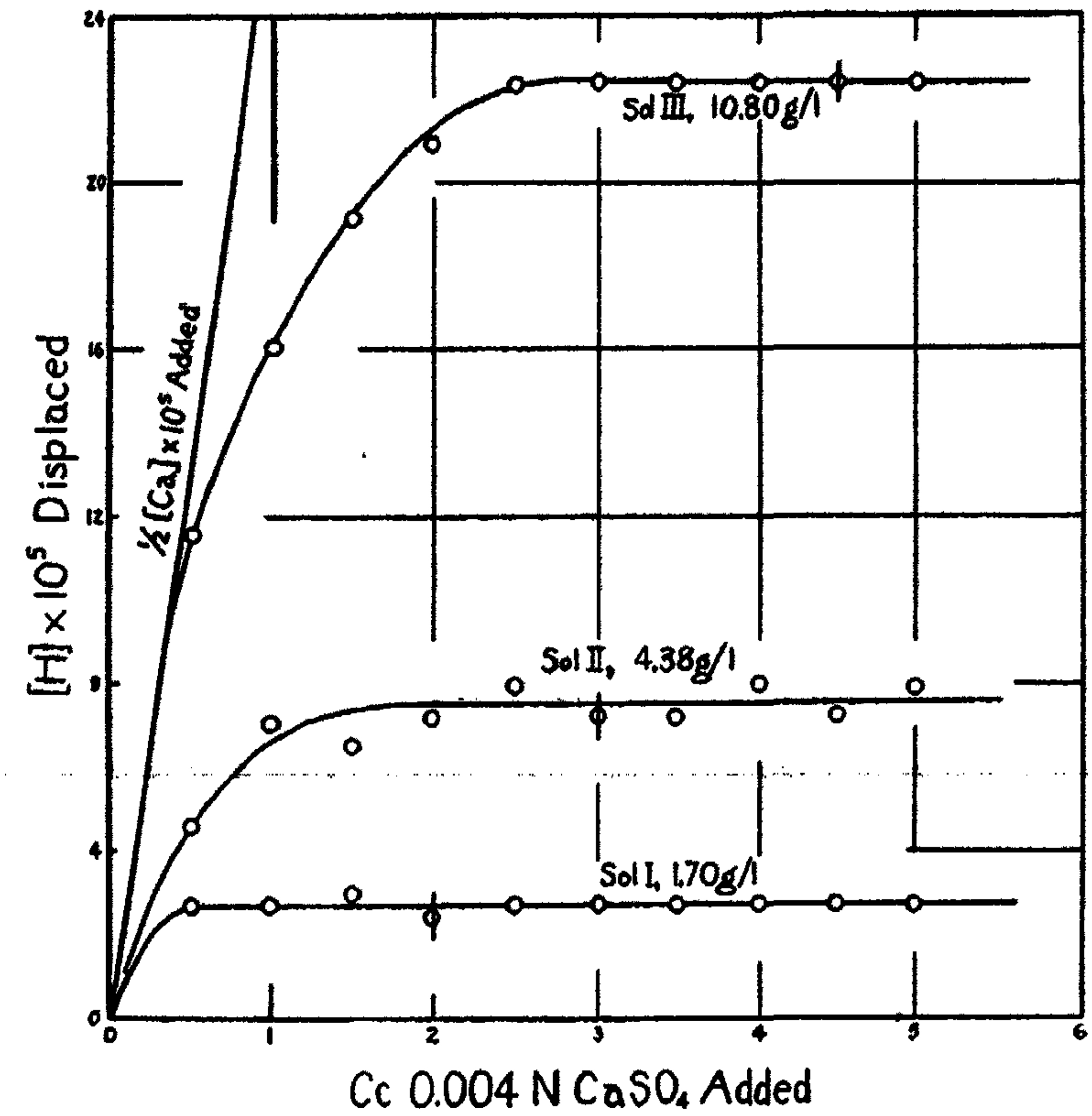

Fig. 1

Hydrogen Ion Displacement Curves for As_2S_3 Sols of Different Concentrations

observation that the cataphoretic migration velocity attains a minimum value well below the precipitation concentration of $BaCl_2$ but not of $AlCl_3$. Except with low concentrations of electrolyte and concentrated sols, the amount of hydrogen displaced is distinctly less than the amount of calcium added.

The total displaced hydrogen is 20%, 21% and 31% of the total hydrogen in the filtrate after coagulation of sols I, II and III, respectively.

C. Displacement of Hydrogen Ions and Adsorption of Cations

I. Observations on As_2S_3 Sol IV

Titration Experiments. The above experiments having indicated that a sol containing 10 g/l would show a satisfactory displacement of hydrogen ions, a sol of approximately this composition (10.64 g As_2S_3 per l) was prepared and titrated with the chlorides of barium, strontium, calcium, aluminum, and ammonium, employing the method previously described. Most of the titration data for the salts with multivalent cations are given in Table II and all of the data are shown graphically in Fig. 2.

TABLE II

Titration of As_2S_3 Sol IV with 0.004 *N* Solutions of $BaCl_2$, $SrCl_2$, $CaCl_2$ and $AlCl_3$ (10 cc. of sol. Total volume 15 cc. 30°C)

Solution added cc	π milli-volts	pH	[H] × 10^6 in solution	[H] × 10^6 displaced	Equivalents of electrolyte × 10^6, added
		I. $BaCl_2$ E_0 = 157.4 mv			
0.0	120.8	3.36	43.7	0.0	0.0
0.5	115.5	3.28	52.5	8.8	13.3
1.0	113.0	3.24	57.5	13.8	26.7
1.5	110.7	3.20	63.1	19.4	40.0
2.0	108.3	3.16	69.2	25.5	53.3
2.5	107.9	3.15	70.8	27.1	66.7
3.0	107.5	3.14	72.5	28.8	80.0
5.0	106.3	3.13	74.1	30.4	133.3
		II. $SrCl_2$ E_0 = 154.5 mv			
0.0	118.0	3.36	43.7	0.0	0.0
0.5	113.1	3.28	52.5	8.8	13.3
1.0	110.7	3.24	57.5	13.8	26.7
1.5	107.5	3.19	64.6	20.9	40.0
2.0	105.8	3.16	69.2	25.5	53.3
2.5	105.1	3.15	70.8	27.1	66.7
3.0	104.8	3.14	72.5	28.8	80.0
5.0	103.8	3.13	74.1	30.4	133.3
		III. $CaCl_2$ E_0 = 148.6 mv			
0.0	112.6	3.37	42.7	0.0	0.0
0.5	108.0	3.29	51.3	8.6	13.3
1.0	105.2	3.25	56.2	13.5	26.7
1.5	102.3	3.20	63.1	20.4	40.0
2.0	100.5	3.17	67.6	24.9	53.3
2.5	100.0	3.16	69.2	26.5	66.7
3.0	99.5	3.15	70.8	28.1	80.0
5.0	98.4	3.14	72.5	29.8	133.3
		IV. $AlCl_3$ E_0 = 162.0 mv			
0.0	125.1	3.36	43.7	0.0	0.0
0.5	119.0	3.25	56.2	12.5	13.3
1.0	115.9	3.20	63.1	19.4	26.7
1.5	113.9	3.17	67.6	23.9	40.0
2.0	113.2	3.16	69.2	25.5	53.3
2.5	112.8	3.15	70.8	27.1	66.7
3.0	113.4	3.16	69.2	25.5	80.0
3.5	113.1	3.15	70.8	27.1	93.3
4.0	112.3	3.14	72.5	28.8	106.7
4.5	111.6	3.13	74.1	30.4	120.0
5.0	111.3	3.13	74.1	30.4	133.3

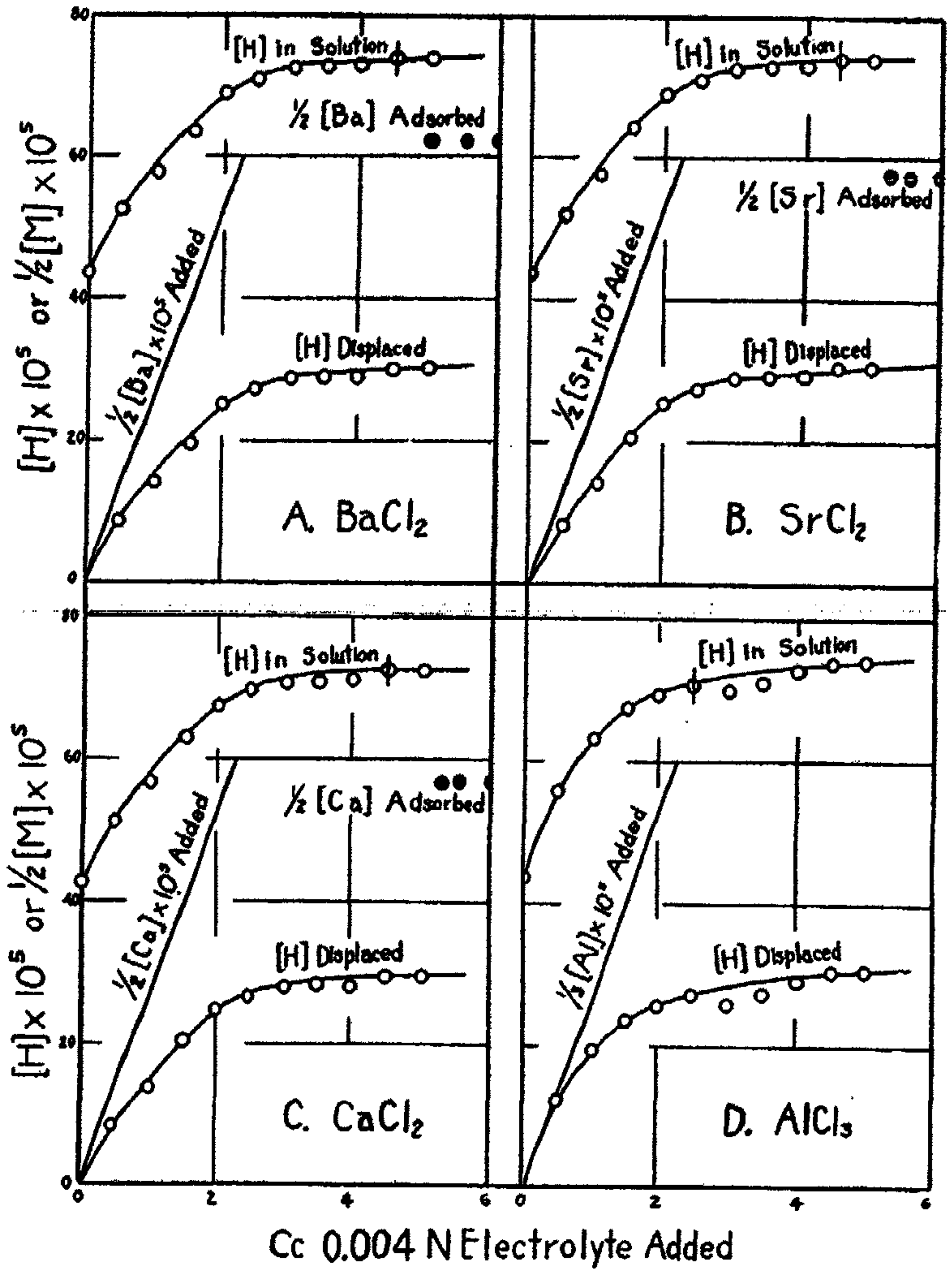

Fig. 2

Titration Curves of As_2S_3 Sol IV. *A* with $BaCl_2$, *B* with $SrCl_2$, *C* with $CaCl_2$, and *D* with $AlCl_3$

Since 5 cc of 0.004 *N* NH_4Cl did not bring about the coagulation of 10 cc of sol, the experiments were continued with 0.01 *N*, 0.04 *N*, and 0.5 *N* solutions. Coagulation occurred on the addition of 1.5 cc of 0.5 *N* solution. The abridged data are given in Table III and Fig. 3. For the same concentration of 0.004 *N* solution the displacement is only one-half as great as with electrolytes having multivalent cations. The increase in the amount displaced after the first 2 cc is quite gradual.

TABLE III

Titration of As_2S_3 Sol IV with NH_4Cl
(10 cc. of sol. Total volume 15 cc. 30°C)

	Cc of NH_4Cl added	π Milli-volts	pH	$[H] \times 10^5$ in solution	$[H] \times 10^5$ displaced	$[NH_4] \times 10^5$ added
		Series I. $E_0 = 150.5$ mv				
	0.0	114.6	3.37	42.7	0.0	0.0
0.004 *N*	0.5	114.2	3.36	43.7	1.0	13.3
	1.0	112.0	3.33	46.8	4.1	26.7
	1.5	110.1	3.30	50.1	7.4	40.0
	2.5	108.5	3.27	53.7	11.0	66.7
	3.0	108.2	3.36	54.9	12.2	80.0
	5.0	106.1	3.23	58.9	16.2	133.3
		Series II. $E_0 = 157.4$ mv				
	0.0	120.7	3.36	43.7	0.0	0.0
0.01 *N*	2.0	113.2	3.23	58.9	15.2	133.3
	3.0	111.6	3.21	61.7	18.0	200.0
0.04 *N*	2.0	109.1	3.17	67.6	23.9	533.3
0.5 *N*	1.5	108.7	3.16	69.2	25.5	5000.0
	5.0	108.1	3.15	70.8	27.1	16666.7

The discussion of these results will be delayed until the adsorption results are given.

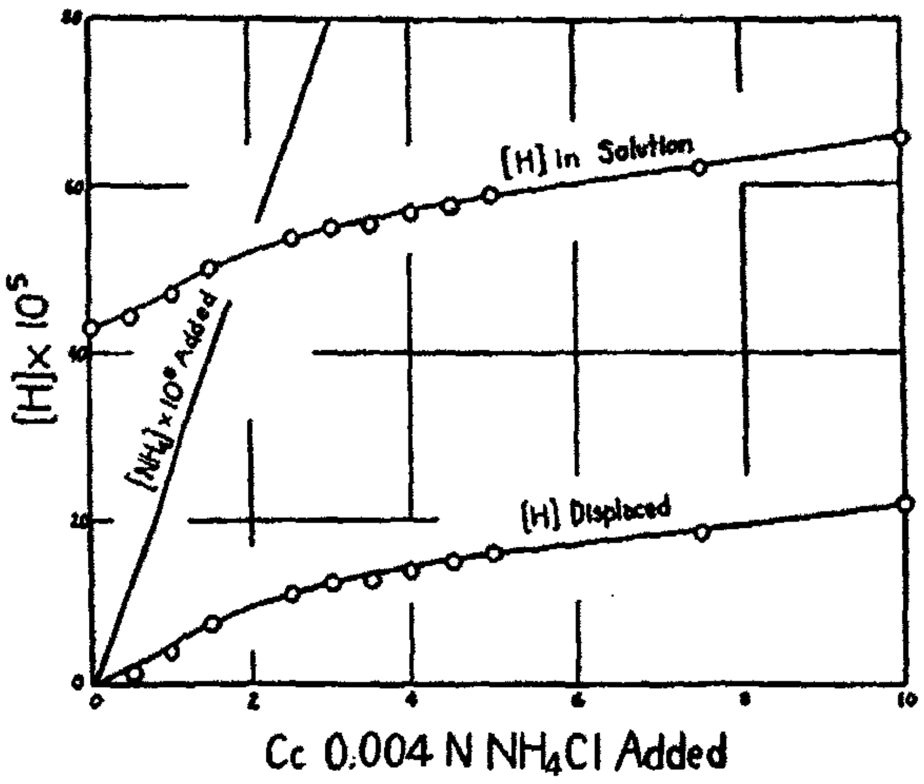

Fig. 3
Titration Curves of As_2S_3 Sol IV with NH_4Cl

Adsorption Experiments. The measurement of the adsorption of cations above the coagulation point was carried out as follows: To 100 cc of sol contained in a wide-mouth bottle, varying amounts of water and 0.01 *N* electrolyte were added, the final volume being 150 cc. After standing stoppered in the dark for 18 hours, the precipitate was matted down by centrifuging and the supernatant liquid filtered through a small filter paper to remove traces of As_2S_3. A 100 cc portion was taken for analysis. The barium and strontium were determined as sulfates and the calcium was precipitated as oxalate and weighed as oxide. For standardization, a sample in which water was substituted for the sol was subjected to the same treatment. The results are given in Table IV and shown on the respective titration curves in Fig. 2. The amounts adsorbed are not quite equivalent, the Ba¨ ion being taken up in slightly greater amount[1] than the Sr¨ and Ca¨. The sol was exhausted before the observations with Al could be made. Later results with another sol show that the adsorption of Al is about the same as that of Ba at a concentration 47% lower than the Ba concentration.

TABLE IV

Adsorption of Ba, Sr, and Ca during the Coagulation of As_2S_3 Sol IV
(100 cc of sol. Total Volume 150 cc)

Cc 0.01 *N* solution added	mg adsorbed	milli-equivalents per g As_2S_3	Equivalents $\times 10^6$ adsorbed	Equivalents $\times 10^6$ added
$BaCl_2$	$BaSO_4$	Ba	Ba	Ba
20.0	11.3	0.091	64.5	133.3
22.0	11.3	0.091	64.5	146.7
24.0	11.3	0.091	64.5	160.0
$SrCl_2$	$SrSO_4$	Sr	Sr	Sr
21.0	8.0	0.082	58.0	140.0
22.0	7.9	0.081	57.3	146.7
24.0	7.9	0.081	57.3	160.0
$CaCl_2$	CaO	Ca	Ca	Ca
21.0	2.4	0.081	57.1	140.0
22.0	2.4	0.081	57.1	146.7
24.0	2.4	0.081	57.1	160.0

Discussion of Results. A comparison of the H˙ ion displacement curves with multivalent ions, Fig. 2, reveals a marked similarity in form. The curves with Ba and Sr are almost identical while the displacement with Ca is distinctly less and with Al greater at low concentrations, than that of Ba. With the divalent ions the displacement curve flattens out before complete coagulation takes place, and the cataphoretic velocity reaches a constant minimum value below the precipitation value of the electrolyte.[2] This may be con-

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[1] Cf. Weiser: J. Phys. Chem., **29**, 955 (1925).

[2] Briggs: J. Phys. Chem., **34**, 1326 (1930).

nected with the relatively slow course of the coagulation in the immediate region of the precipitation value. If sufficient time were allowed, coagulation would probably take place at electrolyte concentrations which give a constant minimum cataphoretic velocity and a constant maximum displacement of H˙ ion. With $AlCl_3$, which precipitates in appreciably lower concentration than the chlorides of the divalent metals, the maximum displacement of hydrogen ion occurs slightly above the precipitation value while the cataphoretic velocity is still on the decrease.[1]

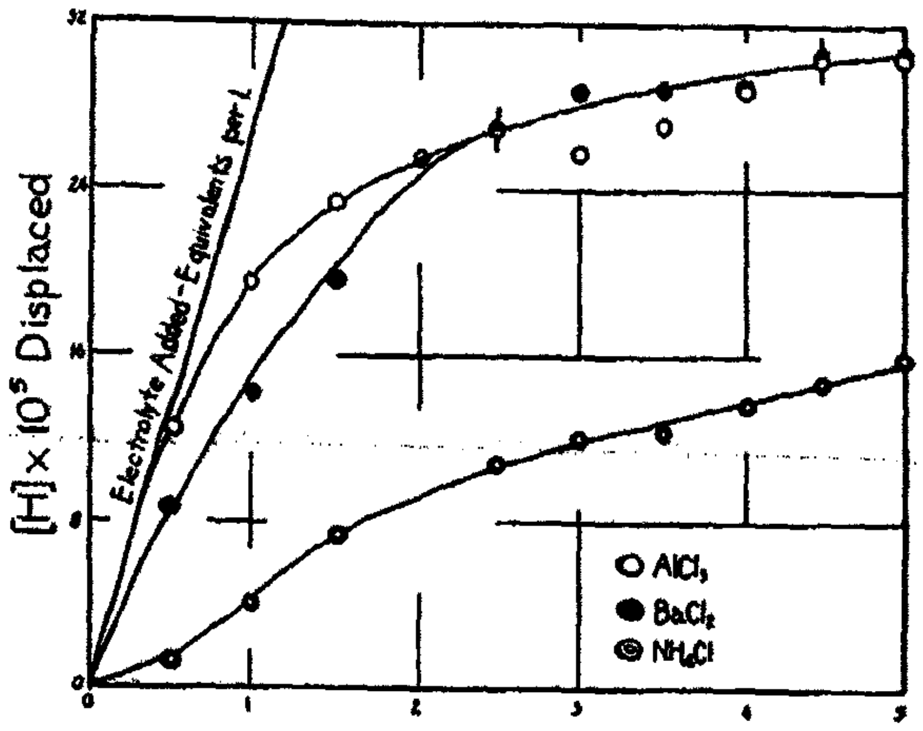

FIG. 4

Hydrogen Ion Displacement Curves of As_2S_3 Sol IV with Cations of Varying Valence

The displacement curves for cations of varying valence are shown in Fig. 4. The marked displacing action of the Al, especially at low concentrations, is in line with the higher precipitating power of $AlCl_3$, while the relatively weak displacing action of NH_4 is in accord with the relatively low precipitating action of NH_4Cl. An analogous behavior was observed with positive sols.[2]

The curves in Fig. 2 show that in the sol under investigation, somewhat more than one-third of the total H in solution after coagulation was displaced from the particles, the remainder being measurable potentiometrically in the original sol. In all cases a portion of the H was derived from H_2S in the intermicellar solution; but even if the solution were saturated with H_2S, this would account for only about 10% of the H˙ ion concentration.

The adsorption of the several cations was approximately twice as great as the hydrogen displaced. This means that a portion of the adsorbed cation corresponds to H measurable potentiometrically in the original sol. The adsorption was from 14% to 22% less than the total H in solution after coagulation instead of being equal to the H˙ ion concentration, as found by Whitney and Ober.

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[1] Loc. cit.

[2] Weiser: J. Phys. Chem., 35, 1, 1368 (1931).

II. *Observations on As_2S_3 Sol V*

As a check on the observations recorded in the previous section, some experiments were carried out with a sol containing 20 g As_2S_3 per liter.

Titration Experiments. Titrations were made exactly as previously described with the chlorides of Al, Ba and NH_4. A portion of the results are given in Table IV and all of them, except for high concentrations of NH_4Cl, are shown graphically in Fig. 5.

TABLE IV

Titration of As_2S_3 Sol V with $AlCl_3$, $BaCl_2$ and NH_4Cl
(10 cc of sol. Total volume 15 cc. 30°C)

	Cc of solution added	π milli-volts	pH	[H] × 10^4 in solution	[H] × 10^4 displaced	Equivalent of electrolyte × 10^4 added
		I. $AlCl_3$ E_o = 148.0 mv				
	0.0	94.1	3.07	8.5	0.0	0.0
0.004 *N*	0.5	90.1	3.01	9.8	1.3	1.3
	1.0	87.4	2.96	11.0	2.5	2.7
	1.5	85.9	2.94	11.5	3.0	4.0
	2.0	85.3	2.92	12.0	3.5	5.3
	2.5	84.4	2.91	12.3	3.8	6.7
	3.0	83.5	2.90	12.6	4.1	8.0
	4.5	82.4	2.88	13.2	4.7	12.0
	5.0	82.7	2.88	13.2	4.7	13.3
		II. $BaCl_2$ E_o = 147.4 mv				
	0.0	93.4	3.07	8.5	0.0	0.0
0.004 *N*	0.5	90.8	3.03	9.3	0.8	1.3
	1.0	87.9	2.98	10.5	2.0	2.7
	1.5	87.3	2.97	10.7	2.2	4.0
	2.0	87.1	2.96	11.0	2.5	5.3
	2.5	85.5	2.94	11.5	3.0	6.7
	3.0	84.2	2.92	12.0	3.5	8.0
	4.0	82.9	2.90	12.6	4.1	10.7
	5.0	82.2	2.88	13.2	4.7	13.3
0.01 *N*	3.0	81.4	2.87	13.5	5.0	20.0
	3.5	81.5	2.87	13.5	5.0	23.3
		III. NH_4Cl E_o = 148.3 mv				
	0.0	94.5	3.07	8.5	0.0	0.0
0.004 *N*	1.0	92.3	3.04	9.1	0.6	2.7
	2.0	90.8	3.01	9.8	1.3	5.3
	3.0	89.2	2.99	10.2	1.7	8.0
	5.0	88.3	2.96	11.0	2.5	13.3
0.04 *N*	1.0	85.9	2.93	11.7	3.2	26.7
	3.0	84.1	2.90	12.6	4.1	80.0
0.5 *N*	0.75	83.6	2.89	12.9	4.4	250.0
	3.0	83.4	2.88	13.2	4.7	1000.0

Adsorption Experiments. The adsorption of Al and Ba was determined by the procedure previously described except that in the case of Al, 250 cc of sol were used and the final volume was 375 cc. A 325 cc sample was taken for analysis and after evaporation to 50 cc, the Al was precipitated with NH_4OH and weighed as Al_2O_3. It seemed impractical to attempt to determine the adsorption of $NH_4^{\cdot}$ ion from change in concentration since the percentage change is so slight compared with the amount required for coagulation. The adsorption data are given in Table V and in Fig. 5.

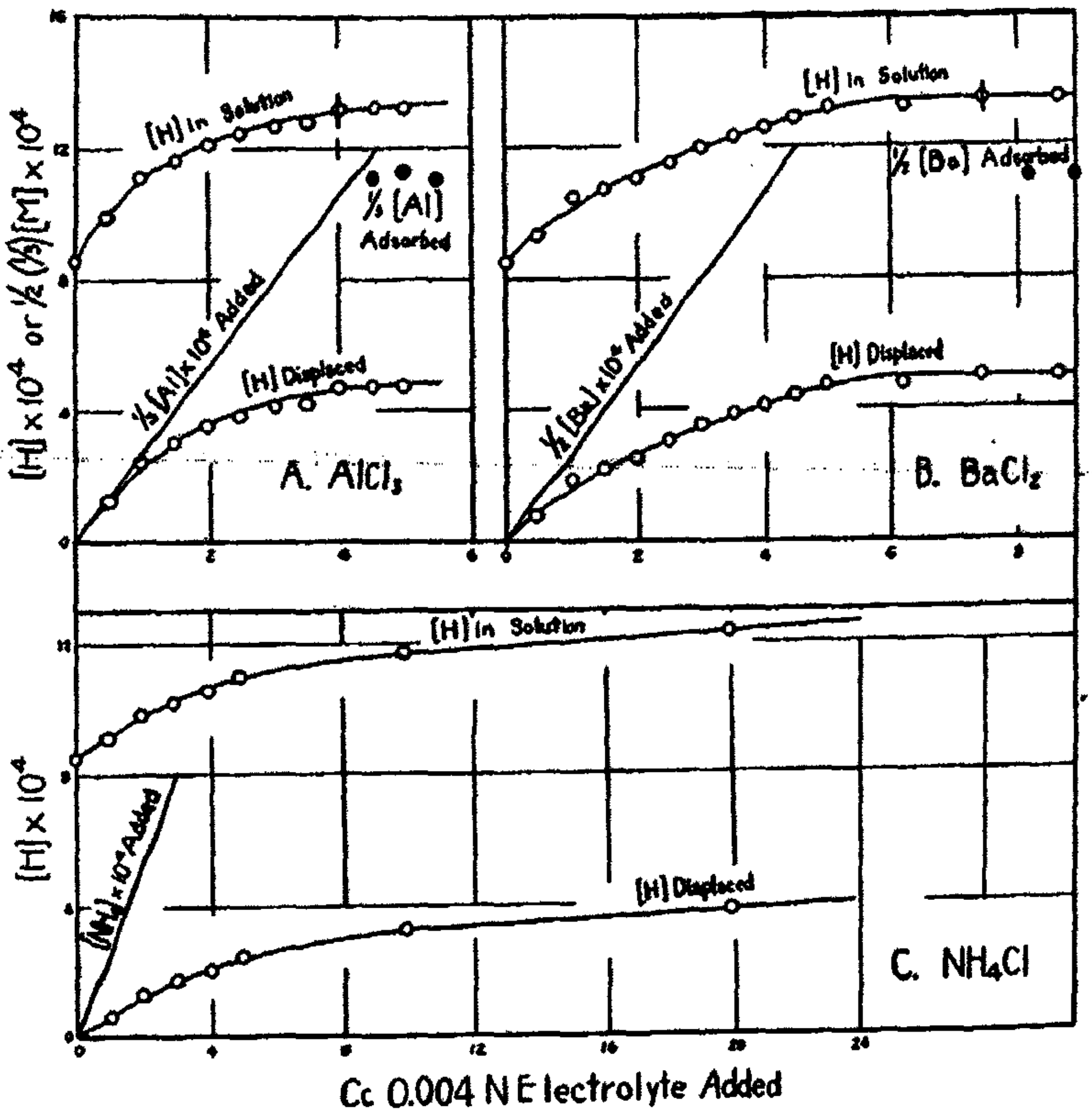

Fig. 5

Titration Curves of As_2S_3 Sol V. *A* with $AlCl_3$, *B* with $BaCl_2$, and *C* with NH_4Cl

Discussion of Results. As would be expected, the titration and adsorption data on the stronger sol V exhibit relationships which are quite similar to those with the more dilute sol IV. The $H^{\cdot}$ ion concentration of the stronger sol is approximately twice that of the weaker but the total hydrogen ions displaced during the coagulation of the stronger sol is only approximately 1.7 times as great as with the weaker sol. This means that relatively more of the $H^{\cdot}$ ions are measurable potentiometrically in the stronger sol than in the weaker. Of the total $H^{\cdot}$ ion concentration in the supernatant liquid after coagulation with

TABLE V

Adsorption of Al and Ba during the Coagulation of As_2S_3 Sol V

Cc 0.01 *N* solution added	mg adsorbed	milli-equivalents per g As_2S_3	Equivalents × 10^4 adsorbed	Equivalents × 10^4 added
(With $AlCl_3$ 250 cc sol. Total volume 375 cc)				
$AlCl_3$	Al_2O_3	Al	Al	Al
45.0	7.1	0.083	11.1	12.0
50.0	7.2	0.085	11.3	13.3
55.0	7.0	0.082	11.0	14.7
(With $BaCl_2$ 100 cc of sol. Total volume 150 cc)				
$BaCl_2$	$BaSO_4$	Ba	Ba	Ba
33.0	19.4	0.083	11.1	22.0
35.0	19.4	0.083	11.1	23.3
36.0	18.7	0.080	10.9	24.0

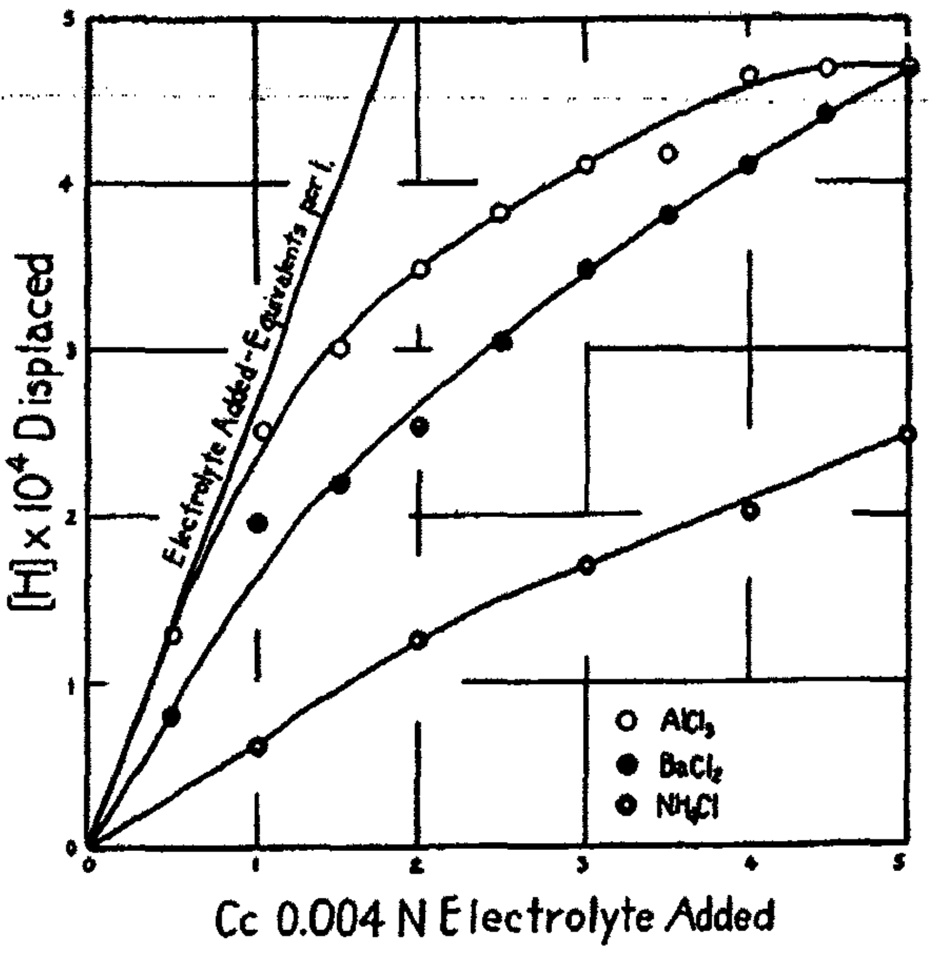

Fig. 6

Hydrogen Ion Displacement Curves of As_2S_3 Sol V with Cations of Varying Valence

divalent ions, approximately 36% was displaced from the colloidal particles as compared with 20% from sol I, 21% from sol II, 31% from sol III and 41% from sol IV. Obviously the amount of displaceable H on the colloidal particle is not determined exclusively by the concentration of the sol but depends on the particle size and the conditions of formation.

The displacement curves for the three types of salts are shown together in Fig. 6. Again it will be noted that at lower concentrations aluminum has a greater displacing power than Ba, and NH_4 a much weaker displacing power than the multivalent ions.

The adsorption of Al and Ba in equivalents is of the same order of magnitude in the region of the precipitation value for the respective salts, but the precipitation value of the Ba is 87% greater than that of Al. From the slope of the H˙ ion displacement curves it appears that the adsorption of Ba is distinctly less than the adsorption of Al at a concentration of $BaCl_2$ corresponding to the precipitation value of $AlCl_3$. Indeed, the adsorption of aluminum is practically complete up to, and including, the precipitation concentration of $AlCl_3$, whereas only one-half the precipitation concentration of Ba is adsorbed.

Constitution of Arsenic Trisulfide Sol and the Mechanism of the Coagulation Process

Since precipitated As_2S_3 is quite hydrous, the composition of the body of the particles may be represented by the general formula $xAs_2S_3 \cdot yH_2O$, the value of x and y being determined by the condition of formation and the age of the sol. The particles are negatively charged and since the chief electrolyte in the intermicellar solution is H_2S, it is probable that the inner portion of the double layer surrounding the particles is chiefly the HS′ ion derived from the primary dissociation of this acid. The anions of arsenious acid or of a thioacid may constitute a portion of this inner layer. The outer portion of the double layer is a diffuse layer of H˙ ions, many of which have sufficient osmotic pressure that they influence the H electrode and can be measured potentiometrically. The constitution of a colloidal particle is represented diagrammatically in Fig. 7. The hydrogen ions within the dotted circle are so firmly held by the attraction of the adsorbed HS′ layer that they do not influence the H electrode. Others with a higher kinetic energy, shown beyond the dotted circle, are measurable potentiometrically with the glass electrode. A small portion of the H˙ ions are derived from the dissociation of H_2S in the intermicellar solution.

On adding an electrolyte such as $BaCl_2$ to the sol the strongly adsorbed Ba˙˙ ions enter the outer layer, displace H˙ ions, and take up a position relatively closer to the inner layer than the H˙ ions, as shown diagrammatically in Fig. 8. This decrease in thickness of the double layer and increase in charge density of the outer layer, result in a lowering of the charge on the particles to the point where collisions result in partial coalescence and agglomeration. Because of the stronger adsorption of the Al˙˙˙ ions the thickness of the double layer is less than with divalent Ba. Accordingly, less Al needs to be adsorbed to reduce the charge to the coagulation point and precipitation takes place with lower concentrations of Al salts than of Ba salts. With the weakly adsorbed ions such as NH_4˙, a relatively high concentration is necessary to increase the charge density in the outer layer and so lower the charge to the coagulation point. Because of the weaker adsorption of NH_4 than of Al and Ba, the displacement of H by NH_4 from the portion of the outer layer represented within the dotted circle is much less than with an equivalent amount of the multivalent ions.

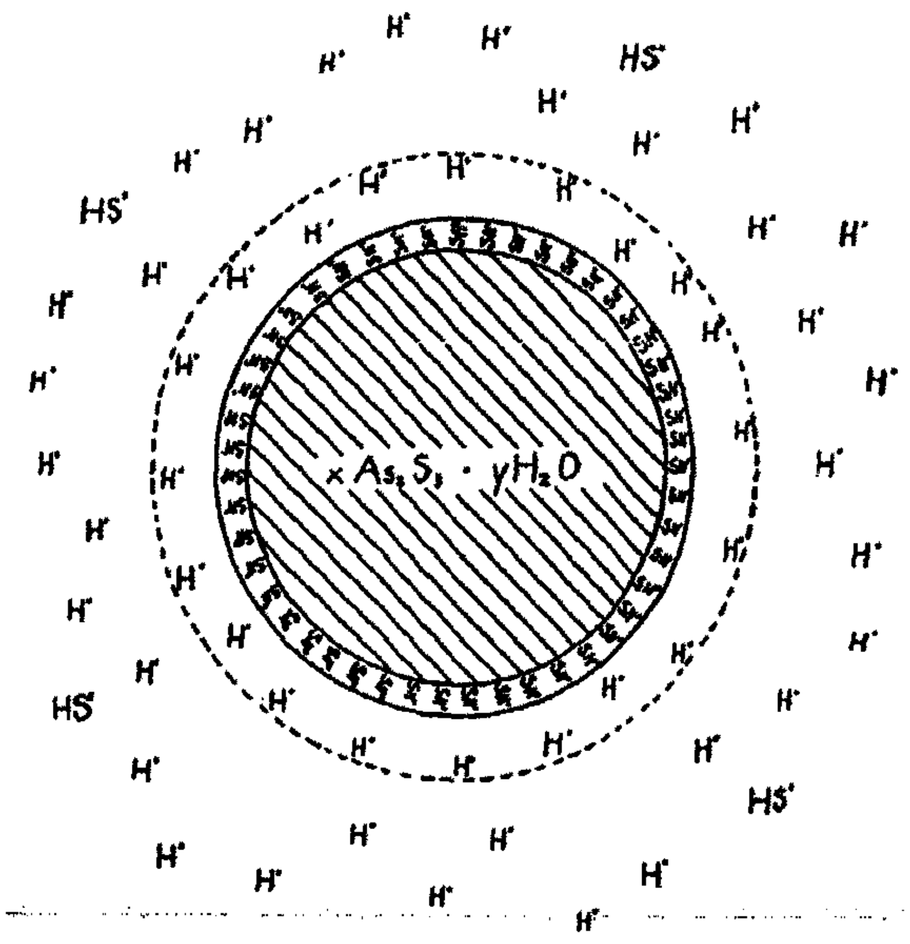

FIG. 7
Diagrammatic Representation of the Structure of the Micelle in the original As_2S_3 Sol

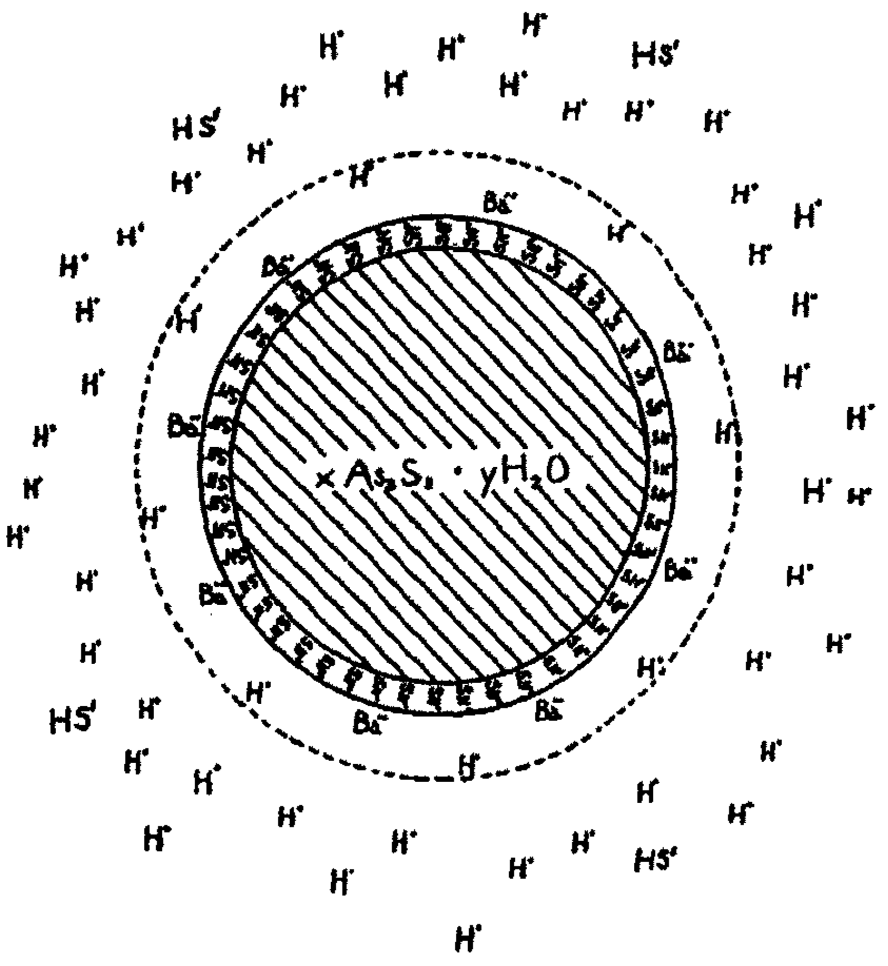

FIG. 8
Diagrammatic Representation of the Structure of the Micelle in As_2S_3 Sol after adding some $BaCl_2$

The adsorption of multivalent cations at their precipitation value is much greater than the hydrogen displaced. The reason is obvious since a part of the adsorbed ion takes the place of hydrogen in the outer portion of the double layer and so increases the charge density of the outer layer. The adsorption is in general less than the total concentration in the filtrate after coagulation. It was a fortuitous combination of circumstances that gave Whitney and Ober a filtrate having the same amount of H˙ ions as the amount of metallic ions adsorbed.

Summary

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

1. Supplementing the classical observations of Whitney and Ober on adsorption during the coagulation of As_2S_3 sol, the glass electrode has been employed in a study of the changes in H˙ ion concentration during the stepwise addition of precipitating electrolytes to the sol.

2. The H˙ ion displacement curve follows a smooth course, similar in form to an adsorption curve. The displacement is relatively greater at lower concentrations and attains a maximum at or below the so-called precipitation value of the electrolytes.

3. In the sols investigated the total amount of displaced H˙ ion varies from 20% to 40% of the total H˙ ion concentration of the supernatant liquid after coagulation of the sol. The amount of displaced H˙ is not determined exclusively by the concentration of the sol but depends on the conditions of formation of the sol as they influence the size and form of the particles.

4. In all cases, the adsorption of precipitating ions is appreciably less than the total H˙ ion concentration of the filtrate after coagulation. The two values will be equal only under a fortuitous combination of conditions.

5. The amount of displaced H˙ is less than the amount of precipitating ion adsorbed. A part of the adsorption corresponds to H˙ in the diffuse outer layer of the particles, which is measurable potentiometrically in the original sol.

6. The order of displacing power of the several chlorides is: Al > Ba, Sr > Ca > NH_4. This is likewise the order of the precipitating power of the several electrolytes and the order of adsorption of the several cations at concentrations below the precipitation value.

7. A diagrammatic representation of the constitution of the colloidal particles is given to account for the above results; and an adsorption mechanism of the neutralization process leading up to coagulation, is outlined.

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GLYCINE IN WATER SOLUTION*

BY JESSIE Y. CANN

A study of the structure of glycine from the absorption spectra of the compound dissolved in water, in hydrochloric acid solution and in sodium hydroxide solution has just been made by Anslow, Foster and Klingler.[1] They also made a study of the freezing points of glycine in water solution. Using their experimental data for freezing points, we, in this paper, have calculated various thermodynamic functions, and have considered glycine as a micelle.

The term micelle, meaning an aggregation of ions or molecules in solution, acting as a unit, has been used by several authors.[2] Hoskins, Randall and Schmidt have studied the activity coefficients of glutamic and aspartic acids. Although these are di-carboxylic acids, the authors assumed that the ionization of the second carboxyl was negligible. Glycine, or amino-acetic acid, has been compared with these acids, considered as micelles, and striking resemblances occur.

Table I contains all the calculated thermodynamic data. The first two columns give the molalities, m, and the freezing point depressions, θ, obtained by Anslow, Foster and Klingler.[1] In column eleven are given the activity coefficients, calculated according to the equations for concentrated solutions given by Lewis and Randall.[3] In the fifth colum are given the values of of $j = 1 - \frac{\theta}{\nu \lambda m}$, where θ = the depression of the freezing point, ν the number of ions assumed at infinite dilution, λ the molecular depression of water i.e. 1.858°, and m the molality. The value for ν was taken as 2, on the assumption that glycine is a uniunivalent electrolyte.

Log j was next plotted against log m, and the values of α and β determined.[3] The value for α was taken as 0.3 and that for β as 0.534. Then j was plotted against log m, and the values of the function $\int_0^m j \, d \log m$ obtained from the areas under the curve, to each of which was added the area from infinite dilution up to molality = 0.01, obtained from the equation,

$$\int_0^{0.01} - j \, d \log m = - \frac{\beta}{2.303\alpha}\left(0.01\right)^{\alpha}$$

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* Contribution from the Chemical Laboratory of Smith College.

[1] Anslow, Foster and Klingler: Unpublished work.

[2] *a.* McBain and Salmon: J. Am. Chem. Soc., 42, 426 (1920); *b.* Randall, McBain and White: 48, 2517 (1926); *c.* Randall and Cann: 50, 347 (1928); *d.* Randall and Cann: Chem. Reviews, 7, 369 (1930); *e.* Hoskins, Randall and Schmidt: J. Biol. Chem., 88, 215 (1930).

[3] Lewis and Randall: "Thermodynamics," pp. 342, 346, 347 (1923).

TABLE I

$\alpha = 0.3 \qquad \beta = 0.534$

m	θ	log m	$m^{\frac{1}{2}}$	$j = 1 - \frac{\theta}{\nu\lambda m}$	$\frac{j}{m^{\frac{1}{2}}}$	log j
0.010	0.029	$\bar{2}.0000$	0.1000	0.2196	2.1959	$\bar{1}.3416$
0.100	0.195	$\bar{1}.0000$	0.3162	0.4752	1.5029	$\bar{1}.6769$
0.210	0.389	$\bar{1}.3222$	0.4583	0.5015	1.0944	$\bar{1}.7003$
0.385	0.710	$\bar{1}.5855$	0.6205	0.5037	0.8118	$\bar{1}.7022$
0.572	1.035	$\bar{1}.7574$	0.7563	0.5131	0.6784	$\bar{1}.7102$
0.765	1.382	$\bar{1}.8837$	0.8746	0.5139	0.5875	$\bar{1}.7108$
0.986	1.769	$\bar{1}.9939$	0.9930	0.5171	0.5207	$\bar{1}.7136$
1.200	2.121	0.0792	1.0955	0.5244	0.4787	$\bar{1}.7196$
1.500	2.679	0.1761	1.2248	0.5194	0.4241	$\bar{1}.7155$

m	θ	$\int_0^m j\, d \log m$	$\frac{j}{2.303}$	$-\log \gamma$	γ	K
0.010	0.029	0.1942	0.0954	0.2896	0.5129	5.40×10^{-3}
0.100	0.195	0.5631	0.2064	0.7695	0.1700	3.48×10^{-3}
0.210	0.389	0.7203	0.2178	0.9381	0.1151	3.14×10^{-3}
0.385	0.710	0.8515	0.2187	1.0702	0.0851	3.05×10^{-3}
0.572	1.035	0.9402	0.2228	1.1630	0.0687	2.90×10^{-3}
0.765	1.382	1.0039	0.2231	1.2270	0.0593	2.86×10^{-3}
0.986	1.769	1.0551	0.2245	1.2796	0.0525	2.87×10^{-3}
1.200	2.121	1.1002	0.2277	1.3279	0.0470	2.78×10^{-3}
1.500	2.679	1.1517	0.2255	1.3772	0.0420	2.76×10^{-3}

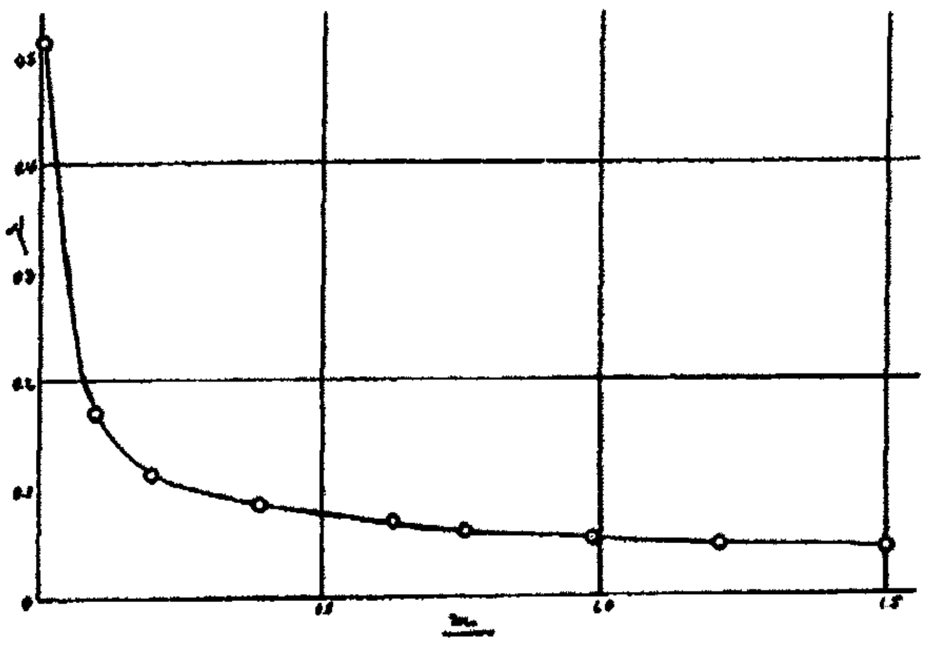
The values for the total areas are given in column ten. Then the activity coefficients, γ, were calculated from the equation,

$$\log \gamma = \int_0^m - j\, d \log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m}\, d\theta$$

The last term was neglected. The values of the activity coefficients are listed in the thirteenth column.

It will be noticed that the values of γ are small, as was to be expected. This is in agreement with the values obtained by Hoskins, Randall and Schmidt[20] for glutamic and aspartic acids. We therefore assume that glycine associates or forms micelles in concentrated solutions. This is also in agreement with the results of Anslow, Foster and Klingler[1] in postulating polymerization in concentrated solutions.

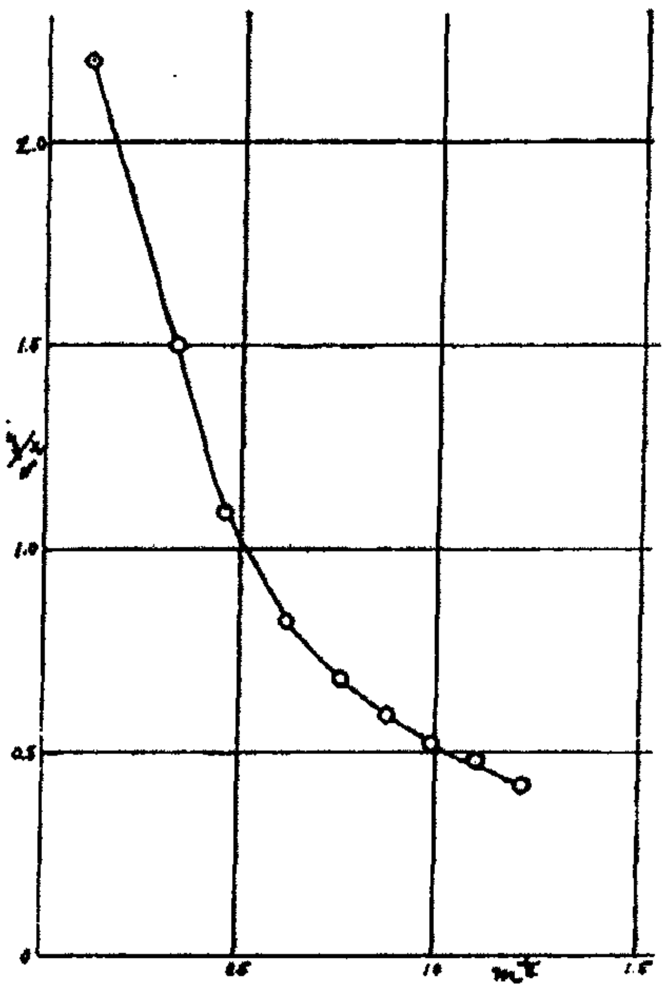
In Curve I we have plotted the values of γ against m. In Curve II we have plotted the values of $j/m^{\frac{1}{2}}$ against $m^{\frac{1}{2}}$. This curve shows that the results



CURVE I

are in agreement with those obtained for other substances by the authors[2] who have assumed micellation. In Curve III we have plotted $-\log \gamma$ against $m^{\frac{1}{2}}$ and find that it can be compared favorably with the composite curve of Randall.[4]

For curiosity, we have calculated values of K on the basis that glycine dissociates in water solution into two ions. We have therefore taken K to be equal to $(m\,\gamma)^2/m(1-\gamma)$. These values are listed in column fourteen of



CURVE II

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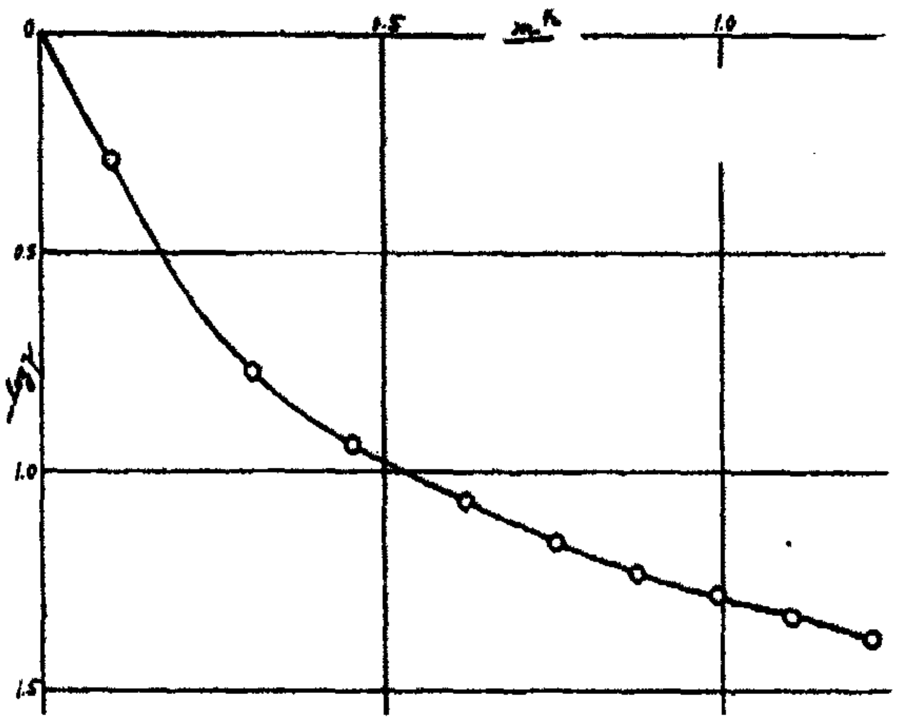
[4] Randall: J. Chem. Educ., 8, 1066 (Fig. 2) (1931).



Curve III

Table I. The values of K_a and K_b, as determined by Branch and Mijamoto,[5] are really hydrolysis constants. They are also considered as such by Adams[6] and by Bjerrum.[7]

The conclusion of this study is that glycine, considered as a micelle in concentrated solutions, shows good agreement with other substances considered thermodynamically on the same basis.

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[5] Branch and Mijamoto: J. Am. Chem. Soc., **52**, 863 (1930).

[6] Adams: J. Am. Chem. Soc., **38**, 1503 (1916).

[7] Bjerrum: Z. physik. Chem., **104**, 147 (1923).

SILICON HYDRIDE, MONATOMIC, OR TRIATOMIC HYDROGEN

BY A. B. VAN CLEAVE* AND A. C. GRUBB†

In a note,[1] G. R. Schultz criticises a paper[2] by one of the authors and his co-workers. Objection was made to the assumption that the active hydrogen studied in this investigation was triatomic. Our critic considers that this activity can be explained in a more plausible manner on the basis of monatomic hydrogen. In the same note and a subsequent paragraph, the statement is made that from the results of his own work no definite assertion can be made *about the existence of either monatomic or triatomic hydrogen.*

In using either explanation, an assumption would have to be made. Experimental evidence seems to indicate that very little monatomic hydrogen exists above 1 mm. pressure. Kaplan[3] found that at 1 mm. pressure, he could not obtain atomic hydrogen in any quantity through a 1.5 cm. glass tube into a bulb. B. Lewis[4] explains the discrepancy between his results and those of Koenig and Elöd[5] on the basis of recombination of atoms. The former employed pressures of 0.04 to 0.1 mm. and the latter workers 10 mm. to 15 mm. Lewis considered that at 15 mm. pressure hydrogen atoms would recombine before reaching the mixing point.

Other investigators have drawn conclusions about the existence of triatomic hydrogen after attempting to repeat and confirm the experimental results of some of the exponents of this theory. In one particular investigation,[6] from the description of the procedure used it is known that confirmation was not possible.

Very rapid advances are being made in theoretical physics and chemistry. But often these advances are the necessary outgrowth of inadequate explanations offered for some experimental fact by the existing theory. Already the latest theories have been found to be inadequate in some cases as pointed out by several investigators.[7] The theory of Heitler and London[8] which was applied to normal atoms in S states may be nearly correct, but for atoms in other states the theory falls short of general application. If atoms are in an excited state Kemble and Zener[9] found that the nuclear symmetry characteristic is a most important factor influencing their interaction. For atoms in P states some investigators find that orbital angular momentum considerations are of importance. The evidence for the existence of a triatomic hydrogen ion, H_3^+, has been confirmed by a number of investigators. However, H. S. N. Massey,[10] after an extensive mathematical treatment of the triatomic hydrogen ion, H_3^+, by methods used by Heitler and London, states:

"The equilibrium separation cannot be fixed with any certainty and it is still doubtful whether we must regard H_3^+ ion as a true homopolar compound

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or a polarization compound. It would appear that the electron pair is not quite strong enough to hold the extra proton."

It seems from this investigation that the existence of the triatomic hydrogen ion, H_3^+, may also be doubtful on the same principles that deny existence to the neutral triatomic molecule. The latest investigator[11] who tries to prove that triatomic hydrogen does not exist would explain all reactions on the basis of silicon hydride. The perfect blank runs repeatedly confirmed during the investigation by Binder, Filby, and Grubb do not support the theory that silicon hydride produced the results that were found. Since the publication of Hiedemann's paper, our former results have been confirmed and extended. A special investigation of blank runs was made. From the discharge the hydrogen was pumped through an ammonia free and very dilute sulphuric acid solution for an hour. Upon adding Nessler's reagent no ammonia like precipitate was formed. Similar runs were made by passing hydrogen from the discharge in contact with a paper dipping into a solution of lead acetate. No sign of a brown color appeared after an hour exposure to the stream of hydrogen. These blank runs were tried repeatedly and in no case did we find any indication of activity that might be attributed to silicon hydride. But during a regular run with the gas passing in contact with plastic sulphur a paper becomes heavily coated with lead sulphide in less than ten minutes. We find no evidence to support the silicon hydride explanation for hydrogen activity and consider it a factor not applicable under our experimental conditions.

During the investigation of the properties of atomic hydrogen, R. W. Wood[12] found that a fragment of tungsten, platinum or thoria became incandescent in a stream of atoms. This test has been used by other workers when studying the properties of hydrogen atoms. We tried this test a large number of times under our experimental conditions and found no detectable heating effect upon the exposed metallic fragment.

On the basis of the amount of sulphide produced in ten minutes during a regular run one would expect considerable heating effect on a metallic fragment if the activity were due to atoms. We have found no evidence to indicate that the activity of hydrogen studied by Binder, Filby and Grubb was due to hydrogen atoms or silicon hydride. Consequently we consider that we are justified in maintaining the original assumption that the activity found is due to triatomic hydrogen.

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THE FARADAY—EFFECT OF SOME UNI-UNIVALENT ELECTROLYTES IN AQUEOUS SOLUTIONS. I

BY E. BUCH ANDERSEN AND R. W. ASMUSSEN

The magnetic rotation of the plane of polarisation is, in analogy with refractive index, specific heat, etc., to a certain extent an additive property so that an atom, which enters a molecule, approximately always gives the same contribution to the molecule's magnetic rotation, independently of the remaining components of the molecule, but often dependent on the kind of link which is formed. As will be known from Perkin's investigations on organic substances, the rotation is sometimes suitable for the settling of problems of constitution.

Whilst the experimental material with respect to organic substances may be considered tolerably complete, this in no way applies to the inorganic compounds. The inorganic substances, whose magnetic rotation has been measured, give the impression of having been chosen by chance or investigated from some special physical point of view.[1] A systematic experimental material on inorganic compounds does not exist.

From the measurements already published it can be seen that the rotation of salts in solutions is approximately determined additively as the sum of the ions' rotation. A mixture of two salts in solution can give a rotation, which is the sum of those of the components. But the constitution has an effect here also, since, if complex salts are formed, the result will be quite different. It would, therefore, seem possible also within the bounds of inorganic chemistry to use this property for the settling of questions of constitution in the chemistry of complex salts.

But, furthermore, the measurement of the magnetic rotation gives information (so far in very implicit form), which can be expected to be valuable for the theoretical understanding of molecular structure. The magnetic rotation of the plane of polarisation is a dispersion phenomenon, a kind of Zeeman effect. And just as the investigation of the Zeeman effect on a spectral line from an atom in a gas gives information about the nature of the stationary states of the atom, between which the transition takes place, so the Faraday-effect in connection with knowledge of the substance's absorption spectrum and dispersion may be an important aid in the study of molecular stationary states.

We have tried in this work to procure some systematical material for a series of simple substances. The investigation covers different compounds of the cations H, Li, Na, Rb, Cs and NH_4 with the anions F, Cl, Br, I, OH, ClO_3, BrO_3 and IO_3. These ions are all diamagnetic in their normal state (more complicated relations supervene with paramagnetic substances, Ladenburg[2]) and,

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[1] Only the work of Jahn (Ann. Physik, 43, 280 (1891)) is of a more surveying character as far as the inorganic material of his paper is considered. Jahn measured a few salts of Li, Na, K, Sr, Cd and Mn, the results being in good general agreement with the corresponding measurements of ours.

[2] Z. Physik, 46, 168 (1927).

since all measurements are made with light from the visible spectrum, they have been carried out in a part of the spectrum far from any absorption bands. We have not had any precision apparatus at our disposal. Our figures are, therefore, to be considered as a survey material and, in consequence of the whole position, intended more for drawing comparisons between these ions mutually than for a profound investigation of the properties of the individual ion.

The rotation of the investigated solutions has been measured for light of wave length 546$\mu\mu$ and with water as standard substance. We have followed the common practice and given as results the "Verdet-constant" (V) of the solutions and the "molecular rotation" (M) of the dissolved substances. M is given with water's molecular rotation under the same conditions as unity. The absolute values for V have been calculated from Verdet's constant for water, which according to Rodger and Watson[1] for Na-light is:

$$V_{\text{water}} = 0.01311 - 0.0_{6}4.t - 0.0_{7}4.t^2.$$

V is here expressed in minutes of arc and t is a temperature between 4° and 98°. As is to be expected V is for diamagnetic substances only in a slight degree dependent on the temperature. According to our measurements with water at 0°C, $V_{546\mu\mu} = 1.183.V_{589\mu\mu}$.

In order to calculate the molecular rotation of a dissolved substance from the measured rotation of the solution it is assumed that the dissolved substance and the solvent act independently of each other, and that the measured rotation is composed additively from the rotation of these two. This assumption leads to the following expression for the molecular rotation of the dissolved substance (with water's molecular rotation equal to 1), when the dissolving medium is water:

$$M = \frac{D_2}{D_1} \cdot \frac{(\mu\, m_1 + m_2)}{d m_1} - \mu$$

where

M is the molecular rotation of the dissolved substances ($M_{\text{water}} = 1$),

$$\left.\begin{array}{ll} D_1 & \text{is the measured angle of rotation for water} \\ D_2 & \text{is the measured angle of rotation for the solution} \\ m_1 & \text{is the molecular weight of water,} \end{array}\right\} \begin{array}{l} \text{with the same layer} \\ \text{thickness, temperature} \\ \text{and magnetic field.} \end{array}$$

m_2 is the molecular weight of the dissolved substance,

μ is the number of gram molecules of water per gram molecule of dissolved substance,

d is the density of the solution (water = 1) at the temperature at which the rotation angle is measured.

It is to be expected that the assumption mentioned above will not hold in every case and it also turns out that the molecular rotations vary with the concentration of the solutions, sometimes even rather greatly.

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[1] Z. physik. Chem., 19, 357 (1896).

Experimental Technique

The apparatus which we used was built up of units procured from a Laurent polarimeter. The polarizing Nicol was fixed in such a way that it could be easily moved and replaced so as to permit the tube to be placed inside the solenoid. When the Nicols were set for complete extinction one half of the field of view transmitted a slight amount of light. The reason for this was that the Laurent polariscope originally had been constructed for the use of sodium light, whereas we used the green mercury line. It was, however, very easy to decide when the two halves of the field of view were of equal colour-intensity.

The polarisation tube was 40 cm long (volume ca. 35 cm^3). It was in nearly the whole of its length (ca. 38 cm) surrounded by a solenoid of copper wire (diameter of wire 1.5 mm). The total copper weight amounted to ca. 20 kg, and the resistance of the solenoid at room temperature was ca. 7 ohm. To obtain fairly large rotation angles for measurement, currents of 20-23 amps. were used, which correspond to effects of 3000-3700 watts. This naturally caused a rapid heating of the solenoid.

In view of the rotations-dependence upon temperature special precautions must be adopted to preserve the solutions at a constant and well-defined temperature during the measurements. The polarisation tube was, for this purpose, surrounded by a jacket with water and chopped ice, since we found, that, under the given conditions, this was the simplest and most effective method of preventing a rise in temperature in the solutions under investigation. All our measurements are therefore taken at 0°C. To prevent condensation of water vapour a stream of dry air was sometimes during the measurements blown over that end of the polarisation tube, which turned towards the observer.

As a source of light a quartz mercury lamp was used and the desired line was isolated from the mercury spectrum by means of a Wratten filter No. 77a (special green Hg-line) and a liquid filter consisting of a solution of 18 g didymium chloride in 50 cm^3 of water in a thickness of 1 cm.

The solutions under investigation were produced from the purest possible materials (eventually after thorough purifying of these) and their concentration determined by analysis (at least two determinations for each solution). The density at 0° was measured by weighing out in a calibrated pycnometer (ca. 15 cm^3).

The optical measurements were made in the following manner. The polarisation tube with the solution was set aside to cool with ice for ca. 1 hour, while care was taken that an abundant quantity of ice was continually present. Thereafter, together with an abundant supply of ice, it was placed in the polarisation apparatus. The current (and with it the strength of the magnetic field) altered its value somewhat rapidly during the measurements, and it was found to be difficult to keep the current constant by means of a variable resistance. We therefore decided to let one observer undertake the adjustment of the optical apparatus, while the other at a given signal read the current in the solenoid on a precision amperemeter. Each solution was measured four times all together (twice by each observer); similarly the zero position of the apparatus was determined twice by each observer before and after every such set of measurements. The rotation angles were first corrected for the rotation of the empty tube (6′), then reduced to the same current, and finally the four single determinations were brought to an average, which is given as result in the table.

The measured rotation angles lay between 18° and 70°. The polarisation apparatus was provided with nonius which allowed the angle to be read with an accuracy of 1′. The alteration of the field strength caused, however, a considerably larger error. For the sake of control, we have repeated the measurements with a number of solutions, and have every time been able to reproduce the results with some few per mille deviations. The error in the measured angles will in general scarcely exceed ½% of the value. An examination of the significance of the remaining sources of error shows that the uncertainty of the final M-values should not exceed 2%.

Results

All our measurements are, as mentioned, carried out at 0°C. Since the rotation of water has been used as unity, we have measured the effect for this substance several times, evenly distributed over the whole period, Table I. We have therewith aimed partly at getting a good determination of this constant and partly at controlling the working conditions.

TABLE I

Water's rotation at 0°C. $\lambda = 546\mu\mu$

20.76°
20.68°
20.69°
20.63°
20.76°

20.72°
20.71°
20.76°
20.74°
20.57°

20.70° ± 0.020°

All these rotation angles are reduced to an arbitrarily chosen but fixed current (i = 100 scale divisions on the amperemeter, corresponding to ca. 19 amps.). The current was as a rule greater during the measurements. From the measurements with water it can be calculated that the reduced rotation angles correspond to a magnetic potential difference of ca. 80,000 Gauss. cm between the ends of the tube or an average field strength of ca. 2,000 Gauss along the tube.

Table II gives the results of our measurements. The letters used have the same meaning as mentioned before. V is the Verdet-constant in minutes of arc. The column "%" gives the solution's percentage contents of the stated substance. The angles are reduced to the same current as for water.

TABLE II

Magnetic Rotation of the Polarisation Plane. 0°C. $\lambda = 546 \mu\mu$

Substance	m	%	μ	d	D_2/D_1	V	M
KF	58.10	45.96	3.791	1.3815	1.0304	0.0160	1.44
KF	—	21.46	11.80	1.2034	1.0242	0.0159	0.99
HCl	36.47	16.22	10.46	1.0826	1.2976	0.0201	4.51
HCl	—	7.612	24.57	1.0402	1.1386	0.0177	4.55
LiCl	42.40	29.31	5.675	1.2403	1.5425	0.0239	4.31
LiCl	—	13.05	15.69	1.0785	1.2198	0.0189	4.72
NaCl	58.46	25.41	9.526	1.2040	1.3845	0.0215	5.16
NaCl	—	12.80	22.10	1.0992	1.1845	0.0184	5.22
KCl	74.56	21.24	15.35	1.1480	1.2227	0.0190	5.41
KCl	—	15.34	22.84	1.1059	1.1643	0.0181	5.57
RbCl	120.96	30.17	15.54	1.2833	1.2469	0.0193	6.09
RbCl	—	21.77	24.13	1.1846	1.1527	0.0179	5.89
CsCl	168.26	59.62	6.325	1.7425	1.5324	0.0238	7.45
CsCl	—	36.27	16.41	1.3779	1.2541	0.0195	7.03
CsCl	—	14.06	57.01	1.1206	1.0816	0.0168	6.51
NH_4Cl	53.50	19.54	12.25	1.0596	1.2918	0.0200	6.31
NH_4Cl	—	12.54	20.71	1.0407	1.1807	0.0183	5.79
HBr	80.93	43.41	5.855	1.4327	2.0053	0.0311	8.63
HBr	—	20.60	17.31	1.1629	1.3952	0.0216	8.85
LiBr	86.86	45.27	5.828	1.4663	2.0043	0.0311	8.73
LiBr	—	23.70	15.52	1.2029	1.4435	0.0224	8.89
NaBr	102.92	40.06	8.543	1.4278	1.7773	0.0276	9.21
NaBr	—	25.58	16.62	1.2407	1.4309	0.0222	9.14
KBr	119.02	33.32	13.23	1.3033	1.4961	0.0232	9.54
KBr	—	24.30	20.58	1.2058	1.3304	0.0206	9.42
RbBr	165.42	45.92	10.81	1.4907	1.5599	0.0242	10.11
RbBr	—	30.94	20.48	1.2882	1.3415	0.0208	10.41
NH_4Br	97.96	26.79	14.86	1.1749	1.4546	0.0226	10.27
NH_4Br	—	20.05	21.68	1.1244	1.3285	0.0206	10.37
LiI*	133.86	23.04	24.82	1.2009	1.6092	0.0220	18.40
NaI	149.92	60.98	5.325	1.8532	3.3585	0.0521	19.41
NaI	—	34.88	15.53	1.3624	1.9691	0.0305	18.95
KI	166.02	51.51	8.674	1.5799	2.4855	0.0386	19.48
KI	—	39.75	13.96	1.3987	1.9797	0.0307	19.85
NH_4I	144.96	55.10	6.555	1.5166	2.8145	0.0437	20.55
NH_4I	—	35.13	14.86	1.2793	1.9488	0.0302	20.04
NaOH	40.01	12.98	14.88	1.1613	1.1754	0.0182	2.43
KOH	56.11	14.78	17.96	1.1474	1.1275	0.0175	2.75
NH_4OH	35.05	10.25	17.03	0.9790	1.0333	0.0160	3.00
$NaClO_3$	106.46	43.26	7.757	1.3771	1.1188	0.0174	3.35
$NaClO_3$	—	23.91	18.80	1.1941	1.0580	0.0164	3.10
$NaBrO_3$	150.92	19.86	33.78	1.1918	1.1304	0.0175	6.21
$LiIO_3$	181.86	28.03	25.90	1.3034	1.3077	0.0203	10.22

* As it was impossible to obtain a colourless solution of LiI this substance has been measured with yellow light ($\lambda = 578 \mu\mu$, $D_1 = 18.027° \pm 0.015°$).

The solutions of sodium and potassium hydroxide were prepared from Merck's reagents in tablets, which should have a specially small content of carbonate. The solutions were analysed immediately after the optical measurements and the stated results give the total amount of alkali calculated as hydroxide. Special investigations showed that the carbonate content in the two solutions was less than 2% of the amount of hydroxide. We have not made any correction for this, since the carbonate-ion and the hydroxyl-ion have almost the same rotation.

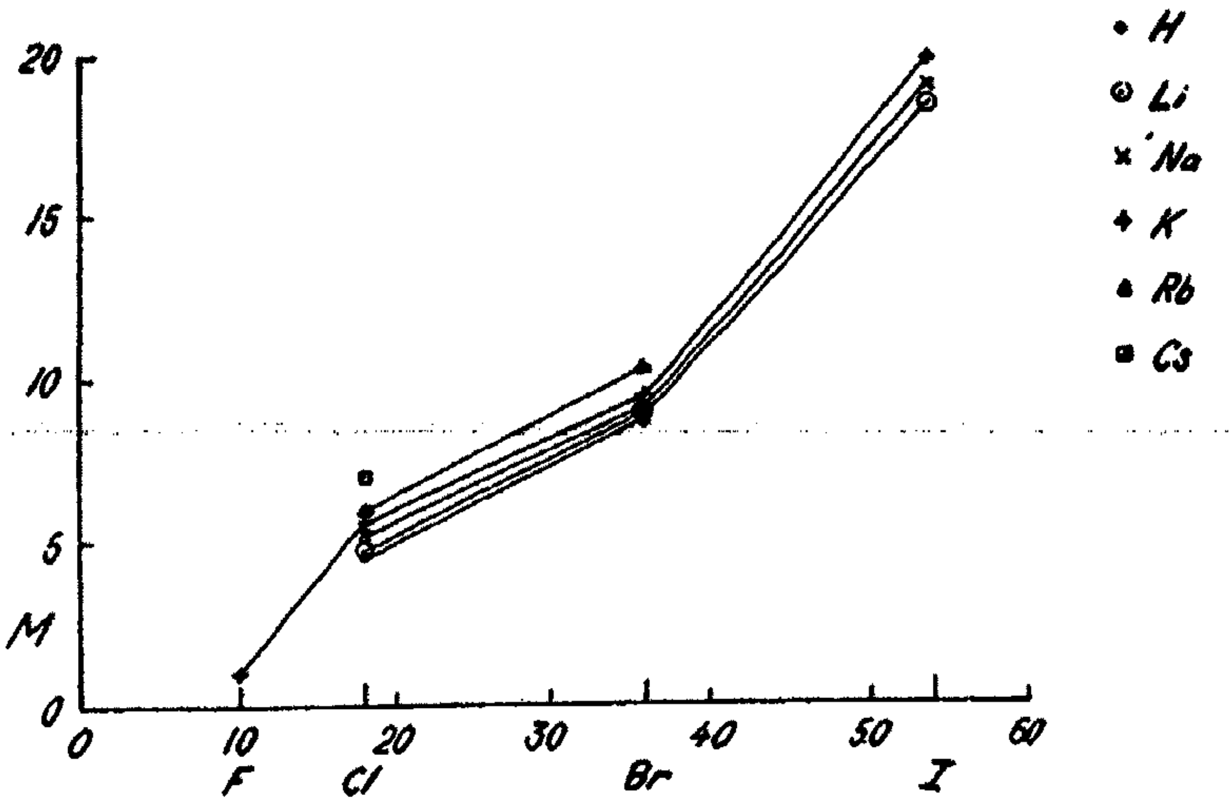

Fig. 1

The $LiIO_3$-solution gave after preparation a slight sediment (probably a basic salt). For this reason we determined the content of both Li and IO_3 in the solution. The Li-content was found to be a little too low in proportion to the amount of iodate (2% of the value). The concentration given in the table refers itself to the amount of iodate, and in the calculation of M we have also followed this, since the rotation of the Li-ion compared with that of the IO_3-ion is very slight.

All substances, investigated in solutions of different concentration, show that M varies with the concentration (in many cases, however, within the error of measurement). The variation is specially large for KF.

In Fig. 1 the results are plotted graphically. Ordinates are the compound's molecular magnetic rotation for green light in solutions with μ equal to 15-25, abscissa the anion's atomic number. It is evident from the figure that the rotation of these compounds can approximately be composed additively by the rotation of the two ions. Further it may be seen that a change of the anion with the same cation gives a large change in the rotation, while change of the cation with the same anion gives only a slight variation in M.

The molecular magnetic rotation of the individual ions can only be computed if the value for one of them is arbitrarily fixed. We can regard the rotation of the hydrogen ion equal to 0. (This would be strictly true if the hydrogen ion in solutions was identical with a hydrogen nucleus). On this assumption the following "ionic rotations" may be computed from our measurements.

TABLE III

Cation	M	Anion	M
H	0.00	F	0.39
Li	0.11	Cl	4.43
Na	0.13	Br	8.97
K	0.60	I	19.04
Rb	1.45	OH	2.15
Cs	2.08	ClO_3	1.76
NH_4	1.00	BrO_3	4.77
		IO_3	10.12

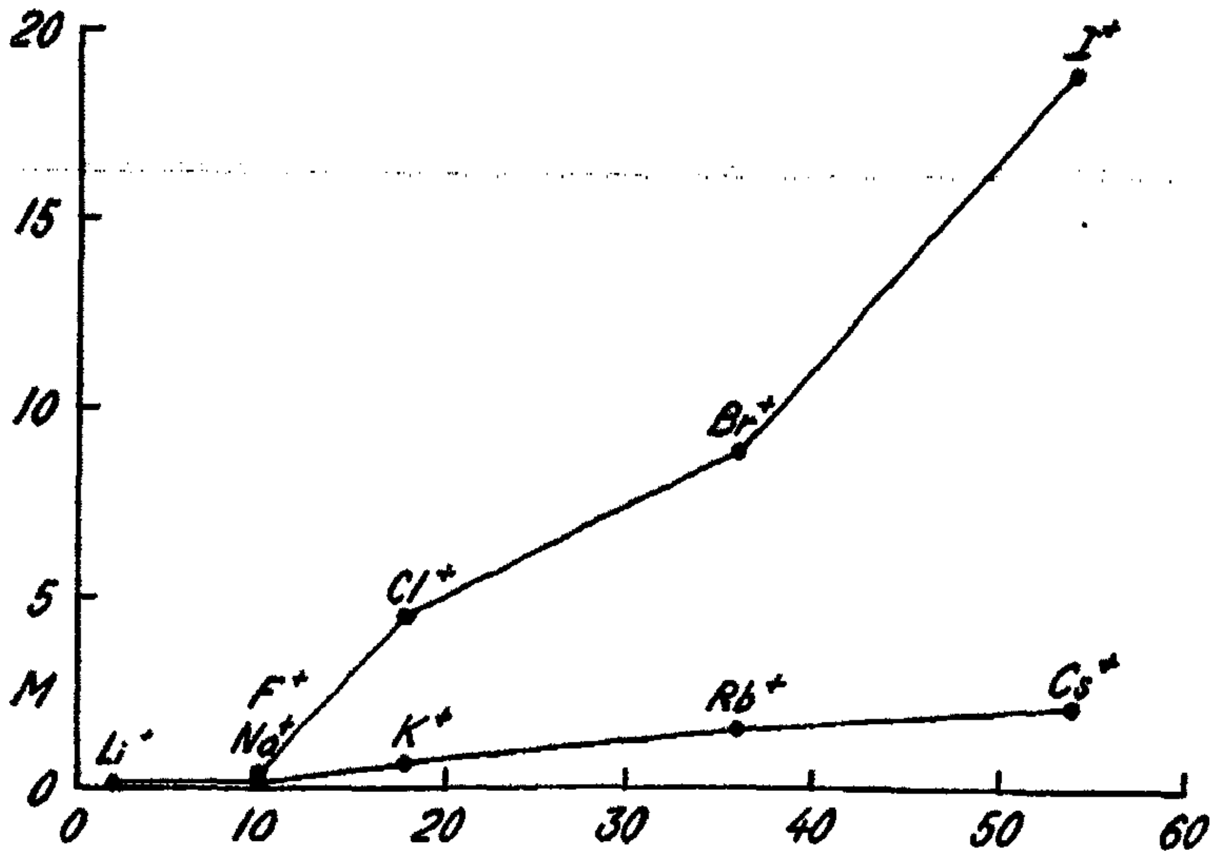

FIG. 2

This table is shown graphically in Fig. 2. The curves correspond completely in form and position to the analogous curves for ionic volumina and refraction. The additive relations are, however, only approximately valid. A test shows that deviations of systematic character appear between the observed values for M and those calculated by means of the table. It must be expected that exact additive relations of this kind only exist for very dilute solutions.

Our figures give some good examples of how the rotation of an individual atom depends upon the kind of chemical linkage. In Table IV is stated how much the molecular rotation of halogen compounds is increased when an atom of chlorine is substituted with bromine or an atom of bromine with iodine. The figures for halides and oxyacids are taken from our own measurements, the figures for organic compounds from earlier determinations of Perkin and others.

TABLE IV

	MX	MXO_3	Org. Comp.
Br – Cl	4.53	3.01	1.83
J – Br	10.07	5.35	4.20

We shall not here attempt to discuss these relations any closer. In conclusion we shall only call attention to a few remarkable facts which have been made evident by the investigation, namely that the rotation of water is nearly one half of the sum of that of hydrogen ion and hydroxyl ion, while a solution of ammonia in water has a rotation equal to the sum of rotations for ammoniumion and hydroxyl ion.

We thank the director of the laboratory, Prof. Dr. Julius Petersen, for his kind permission to use the means of the laboratory for this work.

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THE FARADAY-EFFECT OF ELECTROLYTES IN AQUEOUS SOLUTIONS. II

BY E. BUCH ANDERSEN AND R. W. ASMUSSEN

In the previous work[1] we published measurements of the Faraday-effect for 43 aqueous solutions of simple inorganic compounds. We could demonstrate that the so-called relative molecular rotation of these compounds can approximately be computed by adding together the rotations of the ions in question, which later we determined from the material as a whole, taking the rotation of the hydrogen ion as equal to 0. Our material was comprised of compounds of the cations H, Li, Na, K, Rb, Cs and NH_4 with the anions F, Cl, Br, I, OH, ClO_3, BrO_3 and IO_3.

In the present work we have continued our efforts to bring forth a more systematical inorganic material, having measured the rotation of a further 42 aqueous solutions comprising a number of compounds of alkali-ions with especially sulphurous anions. Besides these, some other compounds have been introduced. The material has been so chosen that it should give information as to how the magnetic rotation of certain compounds will be altered when an oxygen or sulphur atom is added, or when an oxygen atom is replaced by a sulphur atom. In this way is produced a new collection of examples showing the extraordinary importance of the constitution with regard to the magnetic rotation.

Our apparatus is the same as was used in the last work and the earlier treatise contains a detailed description of the experimental technique. All measurements have again been taken at 0°C and for the wavelength $546\mu\mu$. A small alteration in our method of working has been introduced, as we no longer determine the zero position of the polarisation apparatus with each individual measurement. By turning the current in the solenoid the rotation is measured alternately on both sides of the zero-point, the position of this being thus eliminated.

Table I contains the results of our measurements. The first column gives the substance measured. We have, just as in the previous case, used the purest possible substances for preparation of the solutions, which substances have in several cases been subjected to further purification. We prepared some compounds ourselves.

The second column (m) gives the molecular weight of the material measured. The third column (%) gives the percentage of the substance contained in the solutions. The figures have been determined by analysis. Further details about some of the methods of analysis are given below. μ is the amount of g-mol. of water per g-mol. of dissolved substance in the solution. It may be seen from the table that we, in the present work, have been measuring

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[1] J. Phys. Chem., 36, 2819 (1932).

TABLE I

Magnetical Rotation of the Polarisation Plane. 0°C. $\lambda = 546\mu\mu$

Substance	m	%	μ	d	D_2/D_1	V	M
H_2O_2	34.016	30.42	4.319	1.1229	0.9792	0.0152	1.09
H_2O_2	—	15.67	10.16	1.0620	0.9930	0.0154	1.10
H_2O_2	—	10.52	16.06	1.0413	0.9947	0.0154	1.08
H_2S	34.086	0.2303	819.7	1.0000	1.0043	0.0156	5.37
K_2S	110.27	19.23	25.71	1.2084	1.4570	0.0226	12.67
K_2S	—	3.681	160.16	1.0410	1.0811	0.0168	12.52
KCN	65.108	35.39	6.595	1.1869	1.1597	0.0180	3.38
KCN	—	18.66	15.75	1.0973	1.0945	0.0170	3.57
KCN	—	2.883	121.7	1.0184	1.0159	0.0158	3.31
KOCN	81.108	3.905	110.8	1.0259	1.0069	0.0156	2.37
KSCN	97.178	63.65	3.081	1.3925	1.8401	0.0285	8.12
KSCN	—	25.99	15.36	1.1441	1.2934	0.0201	8.10
KSCN	—	4.140	124.9	1.0222	1.0453	0.0162	8.33
NH_4SCN	76.118	21.32	15.59	1.0541	1.2998	0.0202	8.84
NH_4SCN	—	3.276	124.8	1.0076	1.0437	0.0162	8.84
$CO(NH_2)_2$	60.048	5.513	57.13	1.0177	1.0152	0.0158	3.18
$CO(NH_2)_2$	—	2.415	134.7	1.0075	1.0077	0.0156	3.35
$CS(NH_2)_2$	76.118	6.071	65.37	1.0206	1.0979	0.0170	9.17
$CS(NH_2)_2$	—	3.093	132.4	1.0105	1.0516	0.0163	9.79
$SOCl_2$	118.99	100	0	1.6754	2.1827	0.0339	4.66
SO_2Cl_2	134.99	100	0	1.7087	1.3485	0.0209	1.53
H_2SO_4	98.09	3.870	135.2	1.0287	1.0030	0.0156	1.93
$(NH_4)_2SO_4$	132.15	38.25	11.84	1.2321	1.0737	0.0167	4.87
$(NH_4)_2SO_4$	—	5.146	135.2	1.0355	1.0185	0.0158	4.99
$(NH_4)_2S_2O_8$	228.22	30.89	28.34	1.1897	1.0204	0.0158	6.83
$(NH_4)_2S_2O_8$	—	7.867	148.4	1.0445	1.0029	0.0156	6.26
Na_2SO_3	126.07	8.565	74.71	1.0998	1.0977	0.0170	7.24
Na_2SO_3	—	3.475	194.4	1.0528	1.0506	0.0163	6.58
$Na_2S_2O_3$	158.14	29.87	20.61	1.2825	1.3106	0.0203	9.42
$Na_2S_2O_3$	—	6.033	136.7	1.0525	1.0565	0.0164	9.33
$K_2S_2O_3$	190.34	40.64	15.43	1.3687	1.3368	0.0207	9.96
$K_2S_2O_3$	—	7.341	133.4	1.0586	1.0505	0.0163	9.47
$(NH_4)_2S_2O_3$	148.22	56.59	6.311	1.3152	1.5863	0.0246	11.22
$(NH_4)_2S_2O_3$	—	5.875	131.8	1.0350	1.0516	0.0163	10.47
$Na_2S_2O_6$	206.14	8.622	121.3	1.0675	1.0239	0.0159	6.00
$K_2S_3O_6$	270.41	8.859	154.4	1.0607	1.0280	0.0159	9.79
$K_2S_3O_6$	—	8.263	166.6	1.0565	1.0263	0.0159	9.82
$K_2S_4O_6$	302.48	13.60	106.7	1.0932	1.0618	0.0165	13.24
$K_2S_4O_6$	—	12.70	115.4	1.0858	1.0591	0.0164	13.56
$K_2S_5O_6$	334.55	6.737	248.1	1.0832	1.0669	—	16.87
K_2CO_3	138.20	47.79	8.381	1.5114	1.1164	0.0173	3.48
$KHCO_3$	100.11	17.22	26.71	1.1214	1.0214	0.0158	2.68

* The potassium penthathionate solution contains further potassium chloride; refer to text.

solutions decidedly more diluted than in the previous experiments, since both the empiric agreement between the individual measurements and calculation of the probable error have proved the justification of this extension of the field of measurement. We have not yet, however, been able to work with "diluted solutions" as these are understood in physical chemistry.

d is the specific gravity of the solution at 0° in relation to water at 0°. D_2/D_1 indicates the rotation of the solution at 0° relative to that of water at the same temperature and in the same thickness of layer, reduced to the same current in the solenoid. The rotation of water was measured regularly throughout the whole work; Altogether 88 determinations of this quantity have been made. The rotation of each solution was measured from 4 to 8 times (2 to 4 times by each observer), this being divided as a rule on two working days. The figures in the table represent the average of these measurements. The measured (double) angles of rotation were of the order of magnitude 30°-40°. V is Verdet's constant in minutes of arc, calculated as described in our earlier paper. Finally, M is the relative molecular rotation of the dissolved substance, when the molecular rotation of water is fixed equal to 1. The error in the quoted values of M will be ca. 1%.

As to the methods of preparation and analysis we shall give some brief particulars.

H_2S was determined by oxidation with iodine and titration by Volhard's method.

K_2S was prepared by ourselves. The sulphide was determined by oxidation with hypobromite and iodometric titration after the method of Willard and Cake.[2]

KOCN prepared by ourselves, recrystallized from methyl alcohol. Analysis according to Mellor.[3]

$SOCl_2$ *and* SO_2Cl_2. Kahlbaum's preparates. Purified by redistillation.

Na_2SO_3. Analysis by Willard and Cake's method.[2]

$Na_2S_2O_6$. Kahlbaum's preparate, twice recrystallized. Efforts have been made to determine the dithionate by oxidation to sulphate in alkaline solution with hydrogen peroxide or bromine. Neither of these processes gave any quantitative oxidation. Oxidation with potassium chlorate and nitric acid did not take place quantitatively either. We therefore determined the concentration of the solutions by evaporation and drying over an argand-burner.

$K_2S_3O_6$. We tried to produce the salt by Willstätter's method,[4] but this method only gave a small yield of an impure product. The salt used was produced by Raschig's method[5] and recrystallized. By qualitative tests it proved to be free from thiosulphate and other polythionates. Quantitative determinations were undertaken by Kurtenacker and Bittner's method,[6] with methyl-red as indicator. The finished product gave by analysis 100.5% potassium trithionate.

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[2] J. Am. Chem. Soc., **43**, 1610 (1921).

[3] Z. anal. Chem., **40**, 17 (1901).

[4] Ber., **36**, 1831 (1903).

[5] "Schwefel- und Stickstoffstudien," p. 296.

[6] Z. anorg. Chem., **142**, 119 (1925).

$K_2S_4O_6$. Produced by Raschig's method[7] and recrystallized; proved to be free from sulphite, thiosulphate, trithionate and pentathionate, but contained traces of sulphate. Quantitative determinations by Kurtenacker's method[8] on the finished product gave 99.77%.

$K_2S_5O_6$. Produced by Raschig's method.[9] Analytical method analogous to that which was applied to the tetrathionate. The resultant substance contains a considerable amount of potassium chloride, and it turned out to be impossible to remove this quantitatively without a further simultaneous extensive decomposition of the pentathionate. Having a number of times vainly tried to bring about a purification we decided (as the production of the pentathionate is rather protracted) to carry out the optical measurements on a solution which contained both salts. A solution of this kind was produced, analysed and its rotation measured. A definite quantity of potassium chloride was then added to a definite quantity of the solution, and the resultant solution was again analysed and the rotation measured. The molecular rotation of potassium pentathionate was established from these two determinations, and the rotation of the potassium chloride was eliminated by use of the rule of addition.

The figures quoted in the table show some examples of the importance of the constitution with regard to the magnetic rotation. It is, however, only the most outstanding features which will appear, and one dare not draw conclusions of a more extensive sort from this basis. The cause of this lies only in a lesser degree in the errors of measurement, which, as stated, amount to ca. 1% of the M-values. Of much greater importance is the alteration of the molecular rotation with the concentration which, as may be seen in the table, can in some cases amount to 10% of the value of the rotation. Figures of real value for the purposes of accurate comparison should therefore be provided by measuring each individual substance in a larger number of different concentrations and then extrapolate the results to infinite dilution. As far as material exists, M does not, however, in most cases seem to approach any limit within the concentrations which can be treated experimentally.

The following examples of the constitutional influence on the magnetic rotation have been taken from diluted solutions with approximately the same value for μ.

I. Addition of O.	ΔM	I. Addition of O.	ΔM
$H_2O_2 - H_2O$	0.1	$Na_2SO_4 - Na_2SO_3$	−2.7
KOCN − KCN	−0.9	$SO_2Cl_2 - SOCl_2$	−3.2

As the rotation of Na_2SO_4 has not been measured, this has been established from the rotation of $(NH_4)SO_4$, the difference $(NH_4)SO_4 - Na_2SO_4$ being taken as equal to the difference $(NH_4)_2S_2O_3 - Na_2S_2O_3$.

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[7] "S- und N-studien," p. 289.

[8] Z. anorg. Chem., 134, 265 (1924).

[9] "S- und N-studien," p. 276.

II. Addition of S.	ΔM	II. Addition of S.	ΔM
$Na_2S_2O_3 - Na_2SO_3$	2.8	$K_2S_3O_6 - K_2S_2O_6$	3·7
$K_2S_5O_6 - K_2S_4O_6$	3·3	$KSCN - KCN$	5·0
$K_2S_4O_6 - K_2S_3O_6$	3·7		

The rotation of $K_2S_2O_6$ is calculated by means of the difference $K_2S_2O_3 - Na_2S_2O_3$. We observe the fact that the discrepancy in properties which are otherwise often found between the dithionic acid and the polythionic acids does not appear here. With regard to magnetic rotation the dithionic acid falls very nicely in line with the polythionic acids.

III. Substitution of O with S.	ΔM	III. Substitution of O with S.	ΔM
$H_2S - H_2O$	4·4	$KSCN - KOCN$	6.0
$(NH_4)_2S_2O_3 - (NH_4)_2SO_4$	5·5	$CS(NH_2)_2 - CO(NH_2)_2$	6.4

We thank the director of the laboratory, Prof. Dr. Julius Petersen, for his kind permission to use the means of the laboratory for this work.

Chemical Laboratory A.
Royal Technical College, Copenhagen.
April 27, 1932.

ADSORPTION AT CRYSTAL SOLUTION INTERFACES*

VI. Macroscopic Sodium Nitrate Crystals grown in the Presence of Dyes and Other Foreign Materials

BY L. A. WEINLAND, SR. AND W. G. FRANCE

Introduction

One of the major problems engaging the attention of colloid chemists is that of the stability of colloid systems. The factors bringing about and maintaining a more or less stable condition in sols have been studied attentively from all angles. Prominent among these factors has always been the phenomenon of adsorption. Since the term adsorption means a change in concentration at an interface, there is no reason for excluding from this study the important interfaces that exist between crystals and the solutions from which they develop. Especially is this true since it has been shown conclusively that many sols are made up of very finely dispersed particles of a definitely crystalline character. This fact has been established by work on X-ray analysis. Scherrer[1] and Haber[2] found by the use of the well-known powder method of X-ray analysis that dispersed gold showed the same lattice as macro-crystalline gold and that the particles of colloidal zinc sulfide were crystalline in character. This at once suggests that the study of crystal growth, and the various factors influencing the same, have an important bearing on stability.

The present investigation is an extension of the previous work carried out in this laboratory on "Adsorption at Crystal Solution Interfaces," and is concerned with the influence of foreign materials such as dyes, gelatin, and metal salts on the crystal habit of single macroscopic crystals of sodium nitrate.

For full details of methods used in this investigation as well as complete history and bibliography, reference is made to previous articles in this series.[3,4,5,6,7,8,9]

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* In part from the dissertation presented to the Graduate School of the Ohio State University, by L. A. Weinland, Sr., June 1930 in partial fulfillment of the requirement for the Ph.D. degree. Presented before the Division of Colloid Chemistry at the Cincinnati Meeting of the American Chemical Society, September, 1930.

[1] Nachr. Ges. Wiss. Göttingen, 1918, 96.

[2] Haber: Ber., 55B, 1730 (1922).

[3] McBurney & France: J. Am. Chem. Soc., 46, 540-44 (1924).

[4] Eckert & France: J. Am. Cer. Soc., 10, 579-91 (1927).

[5] Keenan & France: J. Am. Cer. Soc., 821-27.

[6] Bennett & France: J. Am. Cer. Soc., 11, 571-81 (1928).

[7] France: Colloid Symposium Annual, 7, 59 (1930).

[8] Lash & France: J. Phys. Chem., 34, 724-36 (1930).

[9] Foote, Blake and France: J. Phys. Chem., 34, 2236-40 (1930).

Experimental Part

Sodium nitrate was chosen for study with reference to adsorption, modification of crystal habit, and growth ratios for the following reasons.

(1) The crystals are relatively stable in air;

(2) The crystallographic data are available;

(3) Being rhombohedral a different form of symmetry is presented than in the previous work.

(4) Statements have appeared in the literature,[10] to the effect that the modification in crystal form of sodium nitrate is due to strongly adsorbed anions. The statement is made that in the presence of nitric acid, because of the strong adsorption of anion, the crystal habit of sodium nitrate is changed. From this and other considerations Saylor believes that the modification of crystal habit by foreign substances may be predicted and that a general rule can be laid down covering all cases of modification by adsorption.

Ideas developed in previous papers of this series are not in accord with this assumption. It was, therefore, thought advisable to continue the study of sodium nitrate, applying the technique and methods used by previous workers in this laboratory.

A good grade of C.P. sodium nitrate was recrystallized once from water, the crystal mass dried and dissolved to make a solution saturated, or nearly so, at room temperature. This saturated solution was poured in a shallow layer in a large crystallizing dish and set away in a place free from temperature changes and air currents. As soon as crystals of sufficient size had formed these were picked out and dried between filter paper. It was later found that the presence of a very small amount of nitric acid (less than 1 per cent) not only fostered the growth of large crystals, but also prevented entirely the troublesome crusting at the surface of the solution and the extensive creeping up the side of the dish. These crystals were of the same composition as the ones grown in the absence of the acid and there was no modification in the crystal habit.

Short lengths of copper wire were sealed into one of the faces of the rhombohedral crystals of sodium nitrate. The wires carrying the crystals were thrust through thin sections of cork stoppers which were notched and fitted into small shell vials containing a saturated solution of sodium nitrate to which the foreign substance had been added.

It was observed that if the crystals were suspended and left in open vials, evaporation was too rapid and considerable distortion in shape occurred. This distortion took the form of enlarged bases and faces covered with ridges, stair-step like formations and attached meal from the surface of the solution. In order to control the growth the vials were placed in a large desiccator along with a three-inch crystallizing dish containing a small amount of concentrated sulfuric acid. In this way the influence of about thirty substances was determined. The results are given in Table I. The formulas for the series of dyes designated by number have previously been published by one of us.[11]

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[10] Saylor: Colloid Symposium Monograph, 5, 49 (1928).

[11] France: Loc. cit.

TABLE I

Effect of Foreign Substances on Crystal Habit of Sodium Nitrate

Quinoline Yellow	Modification
Picric Acid	No modification
Diamine Sky Blue F.F.	Modification
Para Rosaniline	No modification
Ponceau Red	No modification
Fuchsine	No modification
Congo Red	No modification
Naphthol Yellow	No modification
Oxamine Blue	No modification
Gelatin	No modification
Bismarck Brown	Modification
No. 1	No modification
No. 4	Modification
Methylene Blue	No modification
No. 5	Modification
No. 6	No modification
No. 2	No modification
No. 8	No modification
No. 9	No modification
No. 13	No modification
No. 18	No modification

Note: Nos. 3, 7, 10, 11, 12, 15, 16, 17 were all insoluble in sodium nitrate solution. Nitrates of the following metals, lead, silver, mercurous and mercuric mercury, copper, cadmium, bismuth, cobalt, nickel, manganese, zinc, were all tried and found to be without effect.

Nature of Modification

In the few instances in which the crystal habit is modified at all, the modification is of the following nature: The regular faces of the rhombohedron continue to grow perpendicularly, while at the same time there appear at one or more corners of the crystal triangular truncations or octahedral faces. These are never present at the start but are induced artificially through the process of adsorption at these faces. This seems to indicate that a corner of a crystal may be looked upon as the probable locus of a face, but that in the regular processes of growth these faces grow so rapidly perpendicularly that they never attain to any more than a microscopic area. Adsorption slows up the rate of displacement of these faces and since the rate of perpendicular displacement of the regular faces is not interfered with, by the adsorption of the foreign substances, the octahedral faces must of necessity develop.

The displacement of these artificially developed faces relative to that of the regular faces of the rhombohedron was measured and expressed in terms of the growth ratio V_{111}/V_{100}. In previous measurements of growth ratios advantage was taken of the fact that the seed crystals were provided at the outset with all the required faces. However, with sodium nitrate cube faces only were initially present and therefore, the octahedral faces had to be develpoed before the measurements could be made.

This was accomplished by suspending carefully selected crystals in the saturated solution containing the desired concentration of foreign substance. When the octahedral faces appeared on the opposite corners of the suspended crystal it was then carefully orientated in the optical train so that a pair of octahedral faces and a pair of the regular cube faces were directly in the path of the beam of light and sharply focused on the ground-glass finder. An exposure of the film was made every hour, the film removed and developed and measurements were made as fully described in previous papers.[12]

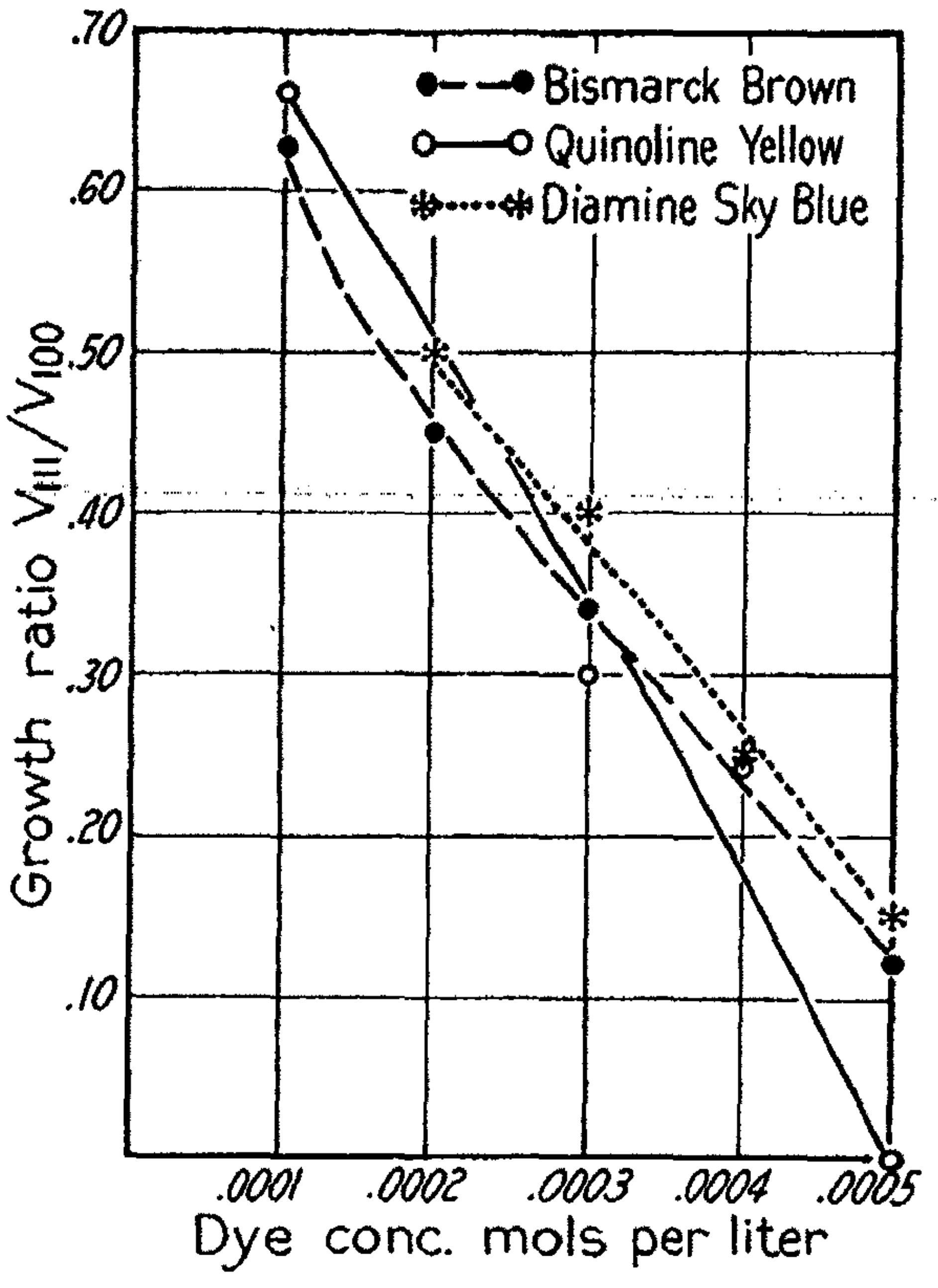

FIG. 1
Growth Ratio-Dye Concentration Curves

One notable change was made in the photographic process. The constant temperature box made of compo board described in previous publications was abandoned in favor of a constant temperature room large enough to contain all of the apparatus and the experimenter as well. The temperature of the room was held at 25°C. by means of a bank of lamps as a heating unit and

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[12] France: Colloid Symposium Annual, 7, 59 (1930).

an automobile radiator through which cold water flowed, as a cooling device. The relays controlling these were actuated by means of a large toluene mercury system. Air was forced through the radiator by means of a fan which was turned off automatically when the lamps were turned on. A large oscillating fan, set behind the lamps, ran constantly and circulated the air in the room. The humidity was indicated by means of a Hare wet and dry bulb hydrometer and was controlled by means of two large shallow trays containing calcium chloride to which water was added as needed.

A summary of the growth ratio data for diamine sky blue, quinoline yellow and Bismarck brown is contained in Table II. Fig. 1 expresses these results graphically. Growth ratios using dyes No. 4 and No. 5 were not determined, due to the irregularity of the octahedral faces which developed in these cases.

TABLE II

Summary of Growth Ratio Data

Table number	Dye	Concentration in mols per liter	Ratio V_{111}/V_{100}
IV	Diamine Sky Blue	.0002	0.50
XIX	Diamine Sky Blue	.0003	0.40
XVIII	Diamine Sky Blue	.0004	0.25
XVII	Diamine Sky Blue	.0005	0.15
III	Quinoline Yellow	.0001	0.66
XX	Quinoline Yellow	.0003	0.30
XII	Quinoline Yellow	.0004	0.24
VIII	Quinoline Yellow	.0005	0.00
X	Bismarck Brown	.0001	0.62
XVI	Bismarck Brown	.0002	0.45
XV	Bismarck Brown	.0003	0.34
XIII	Bismarck Brown	.0005	0.12

X-ray Spectrographs: In order to determine if the adsorption of the dye by the sodium nitrate crystal produced any change in the lattice constant, X-ray spectrographs were made using the powder method. Powder scraped from the faces of a sodium nitrate crystal that was strongly colored by quinoline yellow was placed in one end of the capillary tube and the other filled with powdered pure sodium nitrate. Careful checking of the resulting film revealed the fact that there was no displacement of the lines on the two sides of the median line, and that therefore the lattice constant was unchanged by the adsorption process.

Ultrafiltration: Solutions of the various dyes in saturated alum and sodium nitrate solutions were subjected to the process of ultrafiltration using membranes of collodion. The filtered solutions were examined with the ultra microscope and found to contain relatively few colloidal aggregates. Crystals were grown in these solutions and it was found that exactly the same modification appeared as when unfiltered solutions were used.

Discussion of Results

The effect of those dyes modifying the crystal habit of sodium nitrate is such that faces not normally present are developed in the process of adsorption and growth. These appear as octahedral faces at the corners of the rhombohedron, (a) and (b) Fig. 2. An inspection of the figure, drawn from X-ray data,[13] shows that the octahedral faces are populated by ions of like charge whereas the normally occurring cube faces are made up of mixtures of positive and negative ions. Due to the partial polarization of the residual valencies in the latter one would expect the adsorptive effects to be greater at the octahedral faces The fact that the dyes are preferentially adsorbed on these faces is in harmony with this view. Further support is given by the quantitative results obtained in the measurement of the growth ratios V_{111}/V_{100}. These values decrease from about 0.6 to 0.0 over a dye concentration range of from 0.0001 M to 0.0005 M. The reduction in the velocity of the perpendicular displacement of the octahedral faces together with the accompanying decrease in growth ratios resulting from the adsorption of the dye is in agreement with the conclusion reached in earlier work, that if a foreign material can be adsorbed by a growing crystal the adsorption will in general occur at those planes having the stronger fields of force. This would seem to indicate that one should be able to predict, on the basis of the lattice structure of a crystalline compound the possible variations in habit which would result from the adsorption of a given foreign substance.

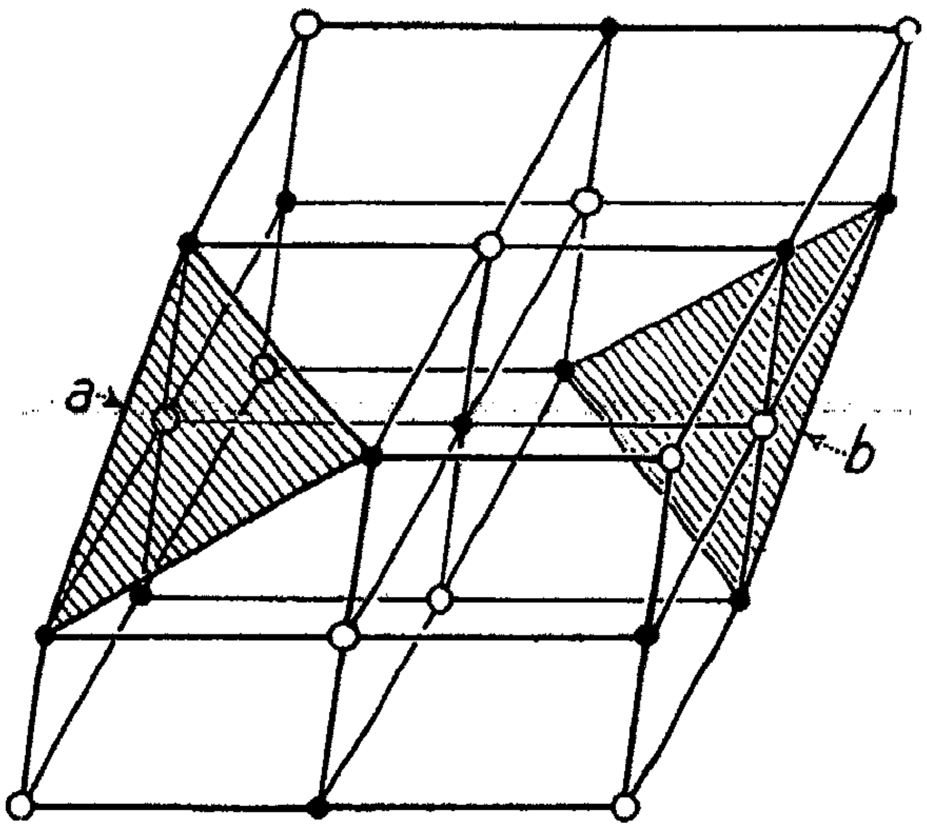

Fig. 2
Arrangement of Na^+,(○) and NO^-_3,(●) ions in Sodium Nitrate rhombohedron

One great difficulty which presents itself is that apparently there is no simple rule that enables one to predict just what foreign materials will be ad-

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[13] Wyckoff: "The Structure of Crystals," 1st Ed. 349 (1924).

sorbed by any one crystalline substance. While comparison of the formulas of those dyes which were adsorbed with those which were not is not especially helpful, such a comparison does, however, show that strongly polar groups are present in all cases where adsorption has occurred. Presumably such groups play an important part in the adsorption process.

The ultramicroscopic examinations and the ultrafiltration of the dye salt solutions appear to indicate that no relation exists between the action of the dyes in modifying the crystal habit and their colloidal state of dispersity.

The X-ray spectographs show that the lattice constant of sodium nitrate is not measurably changed by the adsorption of quinoline yellow. A similar result was obtained in previous work with potassium alum and diamine sky blue. These results indicate that the adsorption occurs interstitially rather than as individual planes or by the replacement of the ions of the unit cell. Further work is at present under way in order to determine the validity of this conclusion.

Buckley[14] has made an extensive study of habit variation of crystals produced by slow and rapid crystallization and by added impurities. These impurities consisted for the most part of ions of the RO_4'' and related types. His investigations involved the production of various crops of crystals and the classification of the individual crystals in each crop according to their habit variations. He concludes that the RO_4'' and related ions which modify the habit of sodium chlorate do so by "taking the place of the ClO_3^- ions." This replacement is believed to be effected by means of the oxygen triangles of the ions. In comparing those ions which were effective with those which were not he comments as follows: "The effective ions by virtue of their shape and the orientation of their attractive force, are able to adhere, while the ineffective ions are probably unable to accommodate themselves to the environment, though in all likelihood, some distortion, compatible with surface adherence of the ion is permissible."

While the substances studied and the methods employed by Buckley are not strictly comparable to those of the present investigation it is nevertheless interesting that similar conclusions regarding the importance of the size and shape of the ions or molecules of the adsorbed materials are reached in both investigations.

Apparently in the absence of exact information concerning the size and shape of ions and molecules and the magnitude of the forces effective at the crystal solution interfaces it is unlikely that accurate predictions can be made, at the present time, as to just what substances any given crystal will adsorb.

Summary and Conclusions

The results obtained in this investigation lead to the following conclusions:

(1) The adsorption of the dyes by a growing crystal of sodium nitrate is dependent upon the residual valency force fields of the crystal face; the inter-

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[14] H. E. Buckley: Z. Krist., **73**, 443 (1930); **75**, 15 (1930); **76**, 147 (1930); **78**, 412 (1930); **80**, 238 (1931); **81**, 157 (1932).

ionic distances within the crystal face; and the presence and distribution of polar groups in the adsorbed molecule or ion.

(2) The adsorption is selective for certain faces, namely those having the stronger fields of force.

(3) The adsorption results in a modification of the crystal habit and a reduction in the growth ratio V_{111}/V_{100}.

(4) With increasing concentration of dye the adsorption becomes greater and the V_{111}/V_{100} values become progressively smaller. This effect continues until a limiting concentration is reached at which the V_{111}/V_{100} value becomes zero and growth stops.

(5) The X-ray data indicate that the dye is adsorbed interstitially. If subsequent work proves this to be general, it will account in part at least for the comparatively small number of substances that are adsorbed by a growing crystal, since, in this event the adsorbed ions or molecules not only would have to possess the required polar properties to satisfy the adsorptive forces of the growing crystal, but would at the same time have to be of the right dimensions to fit into the interstices of the crystal lattice. The number of substances fulfilling both of these conditions simultaneously would naturally be small.

(6) Both the X-ray data and the composition of the dyes render Buckley's explanation for the modification of crystal habit by ions of the RO_4'' and related types inapplicable to the present work.

(7) The adsorption is independent of the colloidal dispersity of the dyes.

(8) These conclusions are in agreement with those arrived at in the earlier investigations of this series.

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THE TRANSFORMATION FROM ROSE TO GREEN MANGANOUS SULFIDE

BY HARRY B. WEISER AND W. O. MILLIGAN

The writers recently[1] criticised certain calculations and conclusions of Mickwitz and Landesen.[2] The validity of the calculations has been upheld by Landesen[3] on the ground that a hydrochloric acid solution which was set down as "n/10" in his Table I (reproduced as Table V in our paper) was not really "n/10." He points out that on page 110 of the paper of Mickwitz and Landesen the exact value was given. The data in question, which Landesen has designated as a "detailed statement" consist of the following: "Gehalt der ständigen Lösungen: 10 ccm $MnCl_2$-Lösung 0.2744 g Mn; 10 ccm HCl-Lösung = 0.4437 g HCl, entsprechend 0.0273 g NH_3."

The data mean that the hydrochloric acid solution was 1.217 *N*. It appeared obvious to us that the solution referred to could not be the one designated in the tables as "n/10." In the light of Landesen's note it now appears that the so-called *N*/10 solution actually used had been prepared from this standard solution by dilution. However no statement regarding the dilution can be found in the original paper, but Landesen states in his note that the solution was used mostly in tenfold dilution, and therefore was not *N*/10. Accordingly the concentration of the acid in Table I should have read 0.1217 *N* instead of *N*/10. Landesen states that he called the 0.1217 *N* acid *N*/10 because of its "proximity" to *N*/10 and for "brevity." Any comment on these extraordinary reasons for designating 0.1217 *N* acid as *N*/10 would be superfluous.

In any event, the important point that we wished to make was that the conclusions of Mickwitz and Landesen are incorrect regardless of the correctness or incorrectness of the calculations. Thus we stated: "But even granting the presence of typographical errors that would account for the discrepancies noted above, the errors inherent in the experimental procedure of Mickwitz and Landesen are too great to enable one to conclude that there is one rose sulfide having the formula $H_2Mn_3S_4$ and one having the formula $(NH_4)HMn_3S_4$."

Landesen also believes that we have stupidly or deliberately misinterpreted some of his statements. He claims that we intimated that Mickwitz and Landesen had "proved and concluded" that rose manganous sulfide will not turn green in the presence of alkali sulfide. What we actually said was: "Favorable conditions for obtaining the green sulfide have been described by a number of people. The experimental procedures were summarized and ana-

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[1] J. Phys. Chem., **35**, 2330 (1931).

[2] Z. anorg. Chem., **131**, 101 (1923).

[3] J. Phys. Chem., **36**, 2521 (1932).

lyzed critically a few years ago by Mickwitz and Landesen. As a result of this analysis and some observations of their own the following conclusions were reached: (1) The transformation from rose to green manganous sulfide never takes place when precipitation is effected with alkali sulfide . . ."

This statement of ours was based on the two following statements in the paper of Mickwitz and Landesen: "The sulfides of potassium and sodium precipitate a rose sulfide which does not go over to the green form."[1] "In the absence of free excess ammonia in the reaction mixture there is no transformation to the green modification from the rose manganous sulfide, freshly precipitated from manganous salt solution with ammonium sulfide."[2]

Landesen is correct in stating that Mickwitz and Landesen record no experiments of their own with sodium sulfide as precipitant; but no one stated that they did. However, in their proposed mechanism for the transformation from the rose to green forms, it is essential that free ammonia be present. Our only contention is that the presence of ammonia is not essential for this transformation, since we showed that the transformation takes place in the presence of sodium sulfide in the complete absence of ammonia, free or bound.

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[1] Mickwitz and Landesen: Loc. cit., p. 101.
[2] Mickwitz and Landesen: Loc. cit., p. 118.

THE USE OF AN ELECTRODE TO STUDY IRREVERSIBLE REACTIONS: THE POLYMERIZATION OF ACETALDEHYDE

BY VINCENT HNIZDA AND D. J. BROWN

Acetaldehyde in presence of acids, salts, and other compounds undergoes polymerization. It has been shown recently[1] that solutions of aldehydes may be used as electrodes showing the variation in voltage for the aldehyde that is formed for reversible electrodes. Hence, we should be able to follow the polymerization by observing the change of voltage of various solutions of acetaldehydes against a standard electrode the same as has been done with reversible electrodes.

The apparatus used and method of measuring was essentially that used by Arenson, Roller, and Brown, except that a Leeds and Northrup student type potentiometer was substituted for the type K, since the former was suitably accurate and could be more rapidly manipulated. All solutions were prepared and kept in absence of oxygen and light except that of ruby lights.

Perchloric acid was purified by distilling under reduced pressure in the presence of barium perchlorate. The distillate was diluted with water and boiled several times to remove nitrates and chlorides. Tests proved that this reduced sulfates and chlorides to less than .00001 normal. More dilute solutions were prepared by diluting with conductivity water, the oxygen removed by boiling under reduced pressure and again diluted to the original mark with "oxygen-free" conductivity water. The diluted solutions were checked with standard alkali solution.

Sulfuric acid, hydrochloric acid, potassium perchlorate, and potassium chloride solutions were prepared by using similar precautions.

The acetaldehyde was prepared by distilling paraldehyde acidified with phosphoric acid in a train of nitrogen. The acetaldehyde was redistilled and kept at 0° C. until used. The aldehyde solution was prepared by distilling under nitrogen the above acetaldehyde below 30°C. measured, diluted with "oxygen-free" conductivity water and kept at 0°C. The diluted solutions were checked by adding sodium sulfite and titrating the sodium hydroxide formed.[2]

The solutions were kept free from oxygen and when required, were forced with nitrogen free of oxygen into burets and then measured into the electrode chamber, and mixed rapidly by bubbling a rapid stream of nitrogen through the solution for one minute. To complete the liquid circuit with the standard electrode the solution immediately was forced into the bridge tube by mercury, which also acted as the metallic conductor. The first reading was observed within two or three minutes from the starting of the preparation of the mixture.

The value for "Equi." equilibrium, is the value obtained after standing 24-72 hours. No further change was observed.

The change of voltage for electrodes in which the molality of perchloric acid is greater than that of the acetaldehyde change similar to that of (a), but

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[1] Arenson, Roller and Brown: J. Phys. Chem., 30, 620 (1926).

[2] Seyewitz and Bordwin: Bull., (5) 33, 1000.

is more positive. The addition of potassium perchlorate has no effect. The effect of sulfuric acid at higher concentrations than acetaldehyde gave results similar to (a).

Representative data for various acids are given here:

t	(a) .10m $HClO_4$ .10m CH_3CHO	(b) .10m HCl .10m CH_3CHO	(c) .10m H_2SO_4 .10m CH_3CHO	(d) .12m $HClO_4$ .70m CH_3CHO	(e) .01m $HClO_4$ 1.6m CH_3CHO
3′	+.275 volts	+.054	+.252	+.290	.335
5	.288	.050	.264	.299	.340
10	.286	.049	.269	.294	.328
15	.286	—	—	.283	.315
25	.285	—	.270	.274	.295
60	.284	.047	.259	.259	.283
100	.286	.047	.258	.236	.282
200	.287	—	.256	—	.267
Equi.	.289	.044	.224	.212	.243

Since all reactions were to be followed electrometrically it was necessary to make the measurements in presence of a conducting solution within the cell. To determine the effects of chlorides each solution was .010 molar perchloric acid and 1.60 molar acetaldehyde except (i) which duplicated (a) above.

t	(f) .010m $HClO_4$ 1.60m CH_3CHO .00001m KCl	(g) .010m $HClO_4$ 1.60m CH_3CHO .0001m KCl	(h) .010m $HClO_4$ 1.60m CH_3CHO .001m KCl	(i) .1m $HClO_4$ .1m CH_3CHO
2′	+.270	+.218	+.159	+.250
4	.277	.220	.157	.265
6	.283	.222	.156	—
9	.287	.220	.157	.270
14	.282	.212	.157	.275
27	.275	.206	.155	.277
80	.259	.198	.156	.280
160	.245	.169	.155	.283
Equi.	.223	.167	.141	.287
				(x) .221
				(y) .111

(x) Indicates that potassium chloride was added to make .001 m. Equilibrium was attained at once.

(y) Indicates that potassium chloride was increased to approximately .01 m. Equilibrium value was attained instantly.

The results indicate that:

1. The measurement of irreversible electrodes while reacting may serve as a tool in determining the course of reactions.
2. The hydrogen ion apparently has a preservative effect on acetaldehyde proportional to its concentration, in fact acts as if it formed a compound.
3. The chloride ion has the effect as if it catalyzed the acetaldehyde polymerization proportionally to its concentration.
4. The apparent equilibrium as indicated by the voltage varies considerably from those of reversible equilibrium relations. This may be due to the fact that the reverse reaction is not catalyzed or that we have no true equilibrium but a metastable condition.

NEW BOOKS

Applied Colloid Chemistry. *General Theory. By Wilder D. Bancroft. Third edition. 21 × 15 cm; pp. ix + 544. New York: McGraw-Hill Book Company, 1932. Price: $4.00.* Eleven years after the publication of the first edition and six years after the second edition, this third revised and enlarged edition of Professor Bancroft's classic work appears with the same general arrangement of material under the following chapter headings: adsorption of gas or vapor by solid: chemical reactions: adsorption of vapor by liquid and of liquid and solid by solid and liquid; adsorption from solution; surface tension-Brownian movement; coalescence: preparation of colloidal solutions; properties of colloidal solutions; electrical properties of colloidal solutions; stability of colloidal solutions; gelatinous precipitates and jellies; emulsions and foams; non-aqueous colloidal solutions; fog; smoke; gases and solids in solids; and thickness of surface films.

Unlike most of the best known books on colloid chemistry, this one is written deliberately and without apology for those "who are interested in colloid chemistry as chemistry rather than as mathematical physics." But colloid scientists of every school will welcome this new edition of what has come to be regarded as a standard work.

The book is a remarkable one in many respects. In the first place it contains an extraordinarily large amount of information systematically and concisely arranged. In the second place, it furnishes the most critical survey of the field that is to be found in any book on this subject in any language. On almost every page a research problem is suggested outright or is hidden between the lines. Finally, with all its multiplicity of critical details, the book is readable and delightfully entertaining. This is because of the author's wide general knowledge, his unquenchable enthusiasm, his ready wit, and his frequent use of homely illustrations to emphasize a point. Few men are gifted with the ability to say and to imply so much in so few words.

Although the subject matter of the book is arranged logically and systematically, it is believed that the volume will be used more widely as a reference book than as a text book for undergraduates. In the reviewer's opinion, the open volume presents too formidable an appearance for a text book. Full pages of uniform printing follow one after another, broken only by an occasional table or figure. Even the references in smaller type which imparted variety to the pages of the earlier editions, have been collected together in the back of the present volume. It is believed that the introduction of numerous section and paragraph headings outlining the contents of the several chapters in bold face type, would enhance materially the appearance of the volume and would add greatly to its usefulness as a text.

In the preface to the first edition which has been reprinted in this book the author writes: "This volume on general theory should be followed by at least one volume on each of the following subjects: silicate industries; paints and varnishes; plastics; fibers and dyeing; photochemistry and photography; petroleum industries; ore flotation and allied subjects; foods and beverages; soils and crops; biology and medicine. Allowing a minimum of three years to a volume, it seems improbable that I shall write all of these single-handed. With the general theory of the subject once cleared up, there is no reason why the other volumes should not be written by people whose knowledge of the special subjects is much greater than my own." It is, of course, too much to expect that Professor Bancroft should complete the series single-handed; but the marked success of his "General Theory" leads us to hope that other volumes will be forthcoming in the not far distant future. However, if he should never write another book, the several editions of "Applied Colloid Chemistry—General Theory" will stand as the greatest single achievement of this generation in bringing the importance of colloid chemistry to the attention of American scientists and industrialists.

Harry B. Weiser

Die gruppentheoretische Methode in der Quantenmechanik. *By B. L. van der Waerden. 25 × 17 cm; pp. vi + 158. Berlin: Julius Springer, 1932. Price: 9 marks.* In the new development of physical theory there has been evident a division of thought between two schools, which seems to be aesthetic rather than scientific. On the one hand there are those whose primary interest is in *things*, who accept any mathematical means, however clumsy, as good enough to lead to an understanding of the subtleties of nature; and on the other there are those whose real enjoyment of the new physics lies in its *form*, its connection with certain beautifully general mathematical ideas. We may compare the two schools, respectively, to those chess players who like to give checkmate with the help of a queen and two castles, and to those who are not content unless their game can produce the position of a chess problem. The present work is of the second type. The very general principles of the theory of groups can be applied to some of the elaborate and troublesome processes of quantum theory, and often make possible a comparatively simple treatment of what otherwise may lead to very complicated formulae.

The present reviewer was rather ignorant of the application of groups of the quantum theory, and approached the book in the hope of gaining a better insight into the connection, but it must be confessed that he was not successful. Though every step in the argument is clearly expressed and readily acceptable, yet at some unknown stage the thread is lost and one found oneself wandering in a maze of half-understood mysteries. The author's style of writing appeared so lucid that it was natural to blame one's stupidity, but a thorough rereading twice and even three times failed to remove the misunderstanding and so the author must surely bear a part of the blame. What is probably the trouble may be illustrated by an example. We all remember as school boys those curiously improbable statements about numbers of apples, or the age of a man and his wife, which led to simultaneous equations. Such problems taught us to deal quite readily with equations such as $5x + 3y = 8$, but the next stage, in which we had to work with $ax + by = c$, was enormously more difficult. If one asked what a was, the answer was that it might be 5, but one was left with the feeling that if it really was 5 it was unfair of the teacher not to call it so all along. The truth of course is that we are all very resistant to general ideas, and only accept them when we have treated so many special cases that we are bored by them into making the generalisation. The trouble with the present book is that though the author does give a few examples, he does not give enough of them to bore us into grasping that there is a single underlying general idea. It seems likely that it is beyond human ingenuity to accomplish the task in such small compass as this book, for its 150 pages have not only to explain group theory, but also to develop the main points of the quantum theory itself.

In conclusion we may express the hope that the author will attempt the task again, but this time with the guiding help of some intelligent ignoramus. It is certainly possible to master the quantum theory without groups, and under these circumstances the ordinary physicist has neither time nor inclination to embark on a full study of general group theory, such as is to be found in works specially devoted to the subject, but would much profit by a work of the present type. The author seems to have all the qualifications for writing such a work, if only he can overcome his simple faith in the rapidity with which the reader can grasp the new train of ideas of group theory. *C. G. Darwin*

Les Statistiques quantiques et leurs Applications. *By Léon Brillouin 24 × 16 cm. pp. 404. Paris: Les Presses Universitaires de France, 1930. Price 125 francs.* That combination of mechanical principles and the laws of probability which we call Statistical Mechanics owes its origin to the desire to explain the laws of Thermodynamics by means of the laws of Dynamics. Its founders were Clausius, Maxwell and Boltzmann. Its first enquiries were directed to the discovery of the way in which the particles of a molecular system will be distributed among the various conceivable positions and velocities at a given time, when the distribution has been given at some original time. Considerable success attended this enquiry for gaseous systems. The next problem to occupy the attention of investigators concerned the phases which succeed one another in a molecular system in the course of time. But the first explicit consideration of the problem which is the central theme of Gibbs' classical work is to be found in Boltzmann's papers. That problem concerns a great number of systems of the same nature, an ensemble of systems, as Gibbs calls it, and their distribution in phase and the permanence or alteration of this distribution in the course of time. Thirty years ago Gibbs wrote in the preface to his "Elementary Principles in Statistical Mechanics"—"In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of Thermodynamics, of radiation and of the electrical manifestations which accompany the union of atoms." In those thirty years the Quantum theory has enriched the province of Mechanics with its special hypotheses, and in correspondence with this widening of our views classical Statistical Mechanics has grown into Quantum Statistics with definite triumphs already to its credit in the regions of enquiry where Gibbs found nothing but doubt and perplexity. A luminous and comprehensive account of this great forward stride will be found in the excellent treatise before us. Originally M. Brillouin wrote it as a volume for the well-known series of French works, "Conferences—Rapports de Documentation sur la Physique." Recently it has been translated into German and published as Number XIII of the excellent monographs published by Julius Springer under the common title: "Struktur der Materie."

In the first two chapters the author begins with the problem of full radiation carrying it as far as classical statistical methods will allow, i.e. to the displacement law of Wien. He signalises at this point the failure of the classical methods to reach the truth as known from experimental effects. "To determine the precise form of the law of radiation one must introduce an additional hypothesis. If the laws of mechanics and electromagnetism are rigorously applied to intra-atomic actions we arrive at the Rayleigh Law of radiation. But this is impossible in practice; the very existence of atoms rests on the new quantum laws and these laws carry with them as a corollary Planck's formula for full radiation."

At this point the author having shown the need for new hypotheses, proceeds in chapter III to develop the concept of the photon in conjunction with relativistic mechanics and the Planck constant. The chapter is devoted to a summary of Louis de Broglie's work and leads to an introduction of Heisenberg's principle of indeterminacy.

The succeeding chapter opens with the following remark. "We have summarised the current ideas concerning the structure of molecules and atoms and pointed out the important part which the 'quanta' play in this connection. We must return to the problem which was raised in the first chapters, namely the study of isothermal radiation. Originally the quanta were introduced by Planck for the purpose of interpreting the experimental laws for black bodies. The hypotheses of Planck were markedly different from those which we have expounded above. It seems indispensable therefore to verify that our point of view will lead us just as well to Planck's formula for radiation. For that purpose, we must recall certain fundamental notions relating to the statistical interpretation of thermodynamics. These definitions of probability were introduced by Gibbs and Boltzmann apropos continuous problems, that is to say concerning bodies or systems capable of passing during an evolution through an uninterrupted series of configurations each of which differs infinitely little from its predecessor and its successor. That is the case with all the usual mechanical systems. But with Bohr's atom we find ourselves faced with a very different problem, so it is necessary to undertake detailed definitions and precise statement of the manner of applying them." This chapter is therefore devoted to a statement of the general definitions of statistical thermodynamics, so framed that they can embrace all the problems of the classical period and still be wide enough to cover the subsequent development of quantum statistics. The notions of quantity of heat, equilibrium state, temperature, entropy, and statistical entropy based on probability are rapidly passed in review and in connection with the latter, the various ways open for the interpretation of "probability." Liouville's Theorem and the ergodic hypothesis lead to the introduction of the canonical ensemble of Gibbs as a basis for the calculation of the probability of states of a system at a given temperature, other than the most probable. This chapter includes an account of the methods of calculating mean values introduced by Darwin and Fowler and concludes with a summary of the formulae of classical thermodynamics and their statistical analogues.

The reader is now in a position to grasp the first innovation of the hypothesis of quanta in statistical calculations—the introduction of the finite elements of extension in phase, or "cells" based on the magnitude of Planck's constant. Chapter V opens with the application of this idea to the stationary light waves which can exist in a reflecting enclosure and the connection between these and the quantised states of the associated photons. This is succeeded by the abandonment of Boltzmann's method of calculating probabilities which assumes that the molecules or ultimate particles of a system can be distinguished from one another; this naturally leads to the Bose-Einstein method where one assumes that any number of representative points may go into one cell, and to the Fermi-Dirac method in which a cell may contain one, but not more than one, representative point or none at all. The appropriate formulae for these two methods are developed, statistical and thermodynamical, and the significance of these results in the case of a degenerate gas is made clear. The connection of the Fermi-Dirac method with Pauli's exclusion principle is pointed out and the important bearing of the latter on the unexpectedly feeble paramagnetism of the usual metals. In the sixth chapter the original problem of the statistics of full radiation with which the book opened is once more taken up and exhaustively treated by means of the concept of the photon and the Bose-Einstein method of counting probabilities. Associated problems concerning fluctuation of energy in an enclosure, emission and absorption of light by an atom and the Compton effect are considered.

One of the most valuable features of the book is the very comprehensive treatment of the electron theory of metals which it contains. For many years the free electron theory has been under a deep cloud of suspicion. Its apparent failure to meet the most obvious requirements of experimental fact—*e.g.* its impotence in face of the now well-known phenomenon of superconductivity—had turned the minds of theorists to other hypotheses for a firm basis for a sound theory. However, a most remarkable change has come over the whole situation during the past five years since the advent of the Wave Mechanics. This new formulation of the mechanical properties of ultimate particles gives a definite support for the application of the Fermi statistical method to systems of electrons and protons. The distinctive feature of this method is the derivation of a distribution function which while agreeing with the usual Maxwell-Boltzmann function for ordinary conditions produces a remarkably different set of deductions for a "degenerate gas." The collection of free electrons in thermal motion in the milieu formed by the lattice of positive ions which is our physical picture of a metal is equivalent to a gas in a completely degenerate state and the appropriate treatment by the Fermi statistics has already dispelled many of the difficulties which we now see were really associated with the classical statistical method. It was not our physical model which was wrong; we were using inappropriate mechanical principles. In chapters VII and VIII of this book all this is explained in an extremely full and lucid manner. All the old troubles concerning the failure of the free electron theory to account for the values of the specific heats of metals vanish; the old calculations of Lorentz improved by these new ideas lead to quite satisfactory results concerning the thermal and electric conductivities. The Pelter, Thomson and Richardson effects, the contact potentials all show signs of fitting into an adequate theory. One important feature of the new method is the apparently paradoxical (on the old views) length of the free path of the electron. To this property around which keen discussion still centres a whole chapter is devoted.

The book concludes with a chapter on the "quantised atom" which contains among other material an account of the basis of those statistical calculations which are employed in discussing dissociation and the anomalous behaviour of electrolytes. There is in addition a mathematical appendix on special formulae and analysis used throughout the work.

J. Rice

Die Quantenstatistik und ihre Anwendung auf die Elektrontheorie der Metalle. *By Léon Brillouin. 22 × 14 cm; pp. x + 530. Berlin: Julius Springer, 1931. Price: 43.80 marks, bound; 42 marks, unbound.* The German edition differs from the French in a somewhat varied presentation of the hypothesis of photons in chapter III, and in the introduction into chapter VIII of some very recent work by the author on the free path phenomena.

It goes without saying that a book of this type cannot be read by anyone not possessing a sufficient mathematical equipment; and it seems to be almost a "fundamental postulate" that the "average" chemist does not possess that equipment; at least that is how the reviewer, who, however, is not a "chemist" in the conventional sense of the term, interprets the sort of conversation he hears in the company of chemists. He sincerely hopes that his interpretation is wrong; for as far as he can see the fundamental problem of the chemist and the physicist is the same; their experimental methods of approach are not merely complementary to one another; they actually in these days overlap in several ways. For the chemist to admit that he cannot for various reasons aspire to the mathematical equipment which the physicist finds he must now acquire is a counsel of despair. As Professor C. G. Darwin remarks in his "New Conceptions of Matter," a new subject "Mathematical Chemistry" is being born, and the chemist must of necessity learn the only language in which the laws and logical methods of an exact science can be expressed. Any chemist who seeks to understand what his own experimental work is revealing to him, must know something of the statistical methods now universally applied in all regions of research on ultimate properties of matter. The work before us will amply repay any effort involved in reading it. It will for instance equip him to follow the application of these new methods to the great problem of molecular combination; the situation there is still involved in difficulty, but there is no doubt that presently simplification will take place, but that simplification will not remove the necessity of knowing something of Quantum Statistics. In Professor Brillouin's work the reader will find all the lucidity of exposition so characteristic of the best French scientific writings.

J. Rice

Il Polarografo, sua teoria e applicazioni. *By G. Semerano. 19 × 13 cm; pp. viii + 207. Padova: A. Draghi, 1932. Price: 16 lire.* This book is a monograph on the dropping mercury cathode, in which the apparatus called the "polarograph" is described. The capillary electrode was originally used by Kucera for electrocapillary measurements analogous to the Lippmann electrometer method. Heyrovsky was the first to measure the current passing through the dropping mercury cathode, and showed that this furnishes a means for qualitative and quantitative analysis. In collaboration with M. Shikata of the Kyoto University he invented the Polarograph, which registers photographically the current-voltage curves, from the shape of which analytical deductions are drawn.

The intention of the author of the monograph is to furnish full information in the technique of polarography. Accordingly in the first part of the book the underlying electrochemical and physical principles are explained, including an original mathematical analysis of the current-voltage curves. Then the applications of the method in inorganic and organic analysis are described. Of analytical importance is the sensibility of the method which is able to estimate matter in the dilution of 10^{-6} gr. equivalents per litre, only a fraction of a cc. being necessary. The investigations of the problems of overvoltage, the mechanism of the dissociation of complex ions and of electro-adsorption at the cathode interface are described. Examples are also given of interest to physiologists, pharmacists and medical chemists. At the end of the book applications to industrial problems are mentioned, viz. in the chemistry of fermentation products, sugar and petroleum. A complete bibliography of 105 papers concludes this monograph, which contains many polarograms and diagrams. The whole subject developed to 1932 is treated exhaustively and the book makes interesting reading not only for those who wish to embark on polarographic research but also for all who are interested generally in electrochemistry.

J. Heyrovsky

Erratum

In the paper by John Frederick James Dippy (**36**, 2354), make the following changes:

p. 2356. The reproduction designated photograph 4 should be photograph 5 and that designated photograph 5 should be photograph 4. On the ninth line from the bottom change (6) to (b).

pp. 2357-8. The reproduction designated photomicrograph 1 (× 30) should be photomicrograph 2 (× 25) and that designated photomicrograph 2 (× 25) should be photomicrograph 1 (× 30).

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THE PARTICLE SIZE OF BIOLOGICAL UNITS. A REVIEW

BY JOHN H. FERGUSON

The biologist has long been accustomed to render to the physical chemist a certain filial respect. This is born of an admiration for the logical method with which observations, carefully performed and accurately correlated, lead to tangible conclusions impressed with the stamp of finality by a successful and practical materialism. Granting the inadequacy of the materialistic viewpoint in the study of living things, it is, nevertheless, just this approach which has raised modern biology to the dignity of a science. The biologist, who has always admitted the handicap imposed by peculiar technical difficulties in controlling his variables—the *milieu* or *environment* as he chooses to term it—now finds the physicist and chemist discarding the old materialism and appealing to mathematics—subtle envoy of metaphysics—for a new "working hypothesis." To let the matter rest on the mathematical formulation introduces an extraneous assumption of *belief*—a philosophical "faith," which a material science has tacitly assumed,[80] pleading the justification not of strict logic but of utility or practical value.

This introductory digression is intended not to encumber the disputation of a scientific topic with the intangibilities of philosophy, but to temper the judgment of the exact sciences upon the methods and results of biological enquiry. The conclusions which are upheld by the faith of biologists rank equally with the "laws" of the material sciences. Every advance in the exact sciences is both a tool and an inspiration to the observer of living things. It is, therefore, both an honour and a privilege to address to physical chemists a consideration of certain data of some quantitative significance from fields of biology which border closely upon their own particular realm. These are fields in which the united physical and biological approach has yielded fruitful results by methods which are now offered for your considerate criticism. The topic is the particle size of such biological units as the filterable viruses, the bacteriophage of the Twort-d'Herelle phenomenon, and the genes which modern biology conceives to be the ultimate physical units of heredity.

It is emphasised that these are borderline cases and not as truly representative of biological phenomena as, let us say, the microscopically visible cell—whether animal, plant, or protist in origin. The problem of their size, therefore, is not synonymous with their claim to be regarded as "living," and this distinction must be borne in mind to the conclusion of our argument.

The Filterable Viruses and Bacteriophage

In 1892, Iwanowski[46] found that the *Mosaic Disease* of tobacco could be transmitted in series by extracts of diseased leaves that had been filtered through bacteria-proof porcelain filters. The discovery was confirmed, independently, by Beijerinck,[14] some seven years later.

It was in 1897 that Loeffler and Frosch[67] aroused the scientific world by the discovery that a similar "filtrate" from the blisters of *Foot-and-Mouth Disease* retains the full potency of the original infective material. No particulate matter could be detected in it by the microscope, or by staining the centrifugate. No visible growth occurred in a variety of culture media.

In 1915, Twort[77] noticed that some bacterial (Staphylococcus) colonies, isolated from a vaccination pock, underwent a destructive or lytic phenomenon, characterised by the appearance, in cultures on solid media, of translucent areas. These areas or "plaques" contained an agent which passed readily through the ordinary bacteriological filters and reproduced the phenomenon in series. It was dependent for its formation and activity upon the actual growth of the susceptible bacterium.

In 1917, d'Herelle[39] recorded a similar phenomenon in cultures of a dysentery bacillus (*Shiga*), broth cultures of which soon had their turbidity cleared up by incubating with a trace of the "filtrate" from the stools of a convalescent patient. d'Herelle has studied the problem, which he has named *Bacteriophagy*, from every angle[37,38]. He has accumulated a large body of data and drawn many conclusions, some of which have aroused considerable controversy.

The hypothesis that the bacteriophage (the question of its plurality need not concern us here) is of a similar nature to the so-called "filterable viruses" is well grounded, and we may conveniently consider them together. Rivers[71] lists some seventy diseases said to be caused by "filterable viruses."

Several conclusions relevant to our present theme now warrant general acceptance. The self-perpetuating agents are exceedingly small. They may be active in dilutions as high as 1:10,000 million. They often pass through high-grade bacteria-proof filters. They are invisible, or at least unresolved, even with a dark-ground microscope which is able clearly to resolve particles of the order of 250 millimicra in diameter.

Nevertheless, they must be regarded as *particulate*. There is a limit of dilution beyond which they do not infect. This cannot be explained away as an insufficiency of dosage, for if, say a cc of a bacteriophagic filtrate is within this limit of dilution, it will dissolve bacteria in a broth culture of any volume —9, 99, or 999 cc, it does not matter which (Gratia and de Kruif[33]). Highly infective virus—or 'phage-containing fluids usually pass through the ordinary bacteriological filters, but not through the finest, such as the higher grade of the Chamberland bougies. Neither do they dialyse through alcohol-ether collodion membranes which permit the passage of water, crystalloids, and certain highly dispersed colloids such as litmus blue.

The formation of isolated "plaques" or bacteriophage is also indicative of a dispersoid nature (d'Herelle,[38] Eijkman[27]). A suspension containing 10,000 million 'phage corpuscles per cc—a "corpuscle" (d'Herelle) being defined as the least quantity which will carry on the phenomena of bacteriophagy—is quite limpid, like the water which forms the continuous phase. It shows, however, the Tyndall phenomenon. In short, we are dealing with matter in the *Colloidal State*, and, in view of the great advances in recent years in the science of colloid chemistry, it is fitting at this time to review our data relating to the probable size of these "living" colloids. We use the term "living" with the diffidence expressed in an earlier paragraph.

The data about to be summarised indicate a *range* of particle sizes of the order of 20–100 mμ, and they have been arrived at by methods which fall into three categories:

1. *Optical Methods*—Especially ultramicroscopy, and the method of photomicrography with very short wave-lengths of "light."
2. *Bacteriological Filtration*—Especially ultrafiltration through collodion gel membranes.
3. *Centrifugation*—As yet little developed in this field.

The Ultramicroscopy of the Filterable Viruses

The applied optics which enters into the theoretical consideration of the possibilities of microscopic technique is largely outside the scope of the present paper. Barnard[4] may be quoted, however, for the following brief résumé of the basic principles:

"Microscopic objects may be divided into two classes, those that are seen by transmitted light, and those that can be made self-luminous. The former are seen as the result of partial or of selective light absorption, that is, they may be semi-opaque, the elements of structure absorbing more or less light, or they may be seen in colour as the result of selective absorption as seen in a stained preparation. For the object to be self-luminous it must be illuminated in such a manner that no direct light reaches the micro-objective, but only that which is refracted, diffracted, or scattered by the object itself. Under these conditions the method is known as dark-ground illumination."

Both methods are subject to the same limitations, which are due to (1) the relative opacity or refractility of the object and the medium in which it is suspended, and (2) the "resolving power" of the optical system. *Resolution* depends upon the microscopic objective—which has now reached the limit of technical achievement in lenses* of N.A. 1.40—and also upon the wave-length of the light used. With ordinary visible light (average wave-length 550 mμ) the "limit of resolution" is reached with objects of 0.2–0.25 micra in diameter. Of course much smaller particles down to 5 or 10 millimicra, or even less[32] may be discerned by ultramicroscopy (Siedentopf and Zsigmondy, 1903[72]), but here we are dealing with "diffraction images" which do not tell us much much about the real nature and size of these sub-resolvable objects. Thus, d'Herelle[37] describes dark-field observations of particles entering the bacterial cell and increasing in numbers when bacteriophagy occurs; but these are not critical observations.

Provided that the increased magnification does not involve an appreciable loss of definition, a slight gain may be expected from enlarging the image by means of high-powered eyepieces. The new trend in microscopy is to employ the short ultraviolet wave-lengths of *light* in conjunction with quartz lenses

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*This is surpassed in mono-bromo-naphthalene lenses.

and a suitable photographic method. The technical details are elaborate and the apparatus is very costly and difficult to use in actual practice. Barnard[4,5] has secured good instruments for working with filtered ultraviolet wave-lengths of 275, 257 and 232 mμ. When the object can be protected against Brownian and the other movement (as in special slide cultures) for a sufficient length of exposure, photographs showing good resolution down to diameters of 50–100 millimicra may be obtained. Working with Gye[34] and others,[5] Barnard has photographed various viruses and bacteria. The aetiological organism of *Bovine-Pleuro-pneumonia*, which is probably the smallest micro-organism definitely seen and cultured, shows a mature "spheroid form," averaging 200–250 mμ in diameter, which buds off young "granular forms" of about half this size. This granular phase is a "filter-passer" (v. infra).

It is claimed that similar, but rather smaller, say, 75 mμ, spheroids and granules represent the causative viruses of the Rous chicken sarcoma, a mouse sarcoma, and even of human carcinoma. The inability of other investigators to confirm these results, especially when more rigid controls are made of the so-called "accessory factor," which is said to be present in ultrafiltrates of the diseased tissue and to be essential for the activity of the "virus," leaves us in doubt as to the true nature of the bodies which Barnard has photographed. Until the crucial experiment has been performed the matter must still remain *sub judice*.

It is of interest to note that recent work lends support to the idea that filterable forms may occur as phases in the life-history of a number of visible micro-organisms, the bacillus of influenza, for instance.

There is a definite limit to the use of short wave-lengths for ultramicroscopy. Just as the shorter wave-lengths of light are extinguished in a fog whereas the longer wave-lengths (the red of a *Neon* sign, for instance) get through, so, too, the use of short wave-lengths in microscopy is limited by the scattering of light by the molecules which make up the lens system, and the refraction image becomes faint and blurred and finally cannot be obtained.

Staining Methods—A priori, would seem to be futile when we can not even see the objects we wish to stain, and, in any case, great caution must be exercised in view of the ease with which one may obtain such artefacts as stain aggregates, protein flocculates, and the like. Two observations may be noted, however. By mordanting and then overstaining with *Giemsa's* stain, fine "granules" may be brought out in certain of the *cell-inclusions* which characterise a number of virus diseases (*e.g.*, Ledingham,[54] 1931). There have also been described peculiar "Globoid bodies" in virus-containing filtrates, whereas controls do not show the same appearances. Bechhold and Villa[12] (1925) describe a special method of impregnation with successive layers of gold sols ("gilding") which is claimed to reveal even the micellae of serum proteins. Bacteriophage (B. Coli) "particles" were estimated by comparative data to have a diameter of greater than 35 mμ and less than 100–200 mμ. Interesting as these results are, they must at present be accepted with reserve.

From the lack of turbidity of 'phage containing filtrates as compared with the well-known milkiness of bacterial cultures (B. Dysenteriae) in fluid media von Angerer[2] (1924) computes for bacteriophage a diameter of less than 20–30 mμ.

Filtration Techniques

Since the method of ultra-filtration, in spite of all its difficulties, has been relied upon more than any other single method for determining the particle size of viruses and bacteriophage, we may allude to the variables *known* to be involved, and the methods whereby they may be controlled.

As with all biological experiments full *controls* must be run throughout. Protocols should include details concerning *animals*, *cultures*, and *media* used: also *apparatus*, and methods of *sterilization*. Sterilizing methods include: (i) aseptic method of preparation, (ii) especially in conjunction with an ultra-violet light chamber (Elford[28]), (iii) autoclaving in alcohol-vapour, which tends to alter the permeability of the membrane, (iv) hot-air sterilization for metal parts, etc.

The Membrane: (a) Composition—is usually acetic-collodion (Bechhold,[9] 1906), or, in Elford's[30] recent formulae (1931), the 'gel' which is deposited by amyl alcohol from an ether-alcohol-acetone solution of nitro-cellulose in such a way as to preserve the "orientation" which gives to ether-alcohol collodion membranes the high grade of uniformity they are known to possess. The lower the percentage of collodion the higher the permeability. Ordinary ether-alcohol collodion membranes are unsuitable because they are quite impervious to viruses and bacteriophage. The siliceous bacteriological filters such as the Chamberland, Berkefeld, Mandler, Seitz, etc. (Mudd[66]) are not sufficiently uniform.

(b) Thickness—should be standardized by a suitable method of depositing layer by layer, or by a roller device such as that of Elford[28] (1929).

(c) Pore-size (average)—may be determined from the permeability to water or to air under pressure. The formulae used for the calculation invoke Poiseuille's law for the flow of fluids through minute channels such as pores or capillaries; (Bechhold,[10,11] Bartell,[6] Hitchcock,[42] Bjerrum and Manegold,[18] and Elford[28]).

(d) Electrical-charge on membrane—may be estimated from its adsorption powers for a range of filterable dyestuffs in buffered solutions.

The Suspension: (a) Electrical charge on the suspended particles can be estimated by cataphoresis (von Angerer,[2] Olitzky and Boëz[68]). The filtration should be conducted with buffered solutions in which the particles have the same sign as the membrane charge so that electro-adsorption is reduced to a minimum. The iso-electric point of foot-and-mouth disease virus, by cataphoretic measurements, is at pH = 8.0, and collodion membranes are negatively charged. Hence an alkaline reaction, pH = 8.5±, is advocated (Olitzky and Boëz[68]).

(b) The Medium in which the particles are suspended is important owing to (1) adsorption and (2) surface tension. Bronfenbrenner[23] showed that a co lodion membrane just impervious to bacteriophage would let it through if washed with broth, but not if washed with saline or a buffered phosphate solution of the same pH as the broth. Elford's[28] method of adjusting the protein content of all suspensions by dilution and the addition of horse serum, has something to recommend it.

(c) The Purity of the particulate agent itself, is a knotty problem, which for all practical purposes must be considered insoluble. There must always be traces of medium, cell-debris, and the like, adsorbed to the particles we are studying. Nevertheless, certain methods of purification which employ cataphoresis in addition to ultrafiltration (Bronfenbrenner[25]) or diffusion into agar (Krueger's modification[53] of Arnold's[3] method) have yielded "purified" bacteriophage preparations free from all traces of protein according to chemical and biological (immunological) tests. The trace of nitrogen still present in Krueger's material is about twice that of the culture medium. Most investigators in the present field have been content to use non-purified material with just a rough preliminary filtration through the coarser ("preliminary") grades of bacteriological filters.

(d) The actual Concentration of the agent we are dealing with, is obviously a matter of conjecture. For bacteriophage we have several methods of comparative determinations, *viz.*, (1) the "serial dilution" method; (2) the "plaque count"; and (3) Krueger's new method,[53] depending upon the time taken to reduce the turbidity of standardized bacterial suspensions to a pre-determined standard. (A limit of error of ±3–5% is claimed for this method.) For viruses we have only the very inaccurate method of the minimal infective dose.

The *Actual Conditions of Filtration* must be strictly uniform.

(a) The Temperature must be constant.

(b) The Time Factor must be controlled, for some organisms, given time enough, may actually grow through bacteriological filters, while others such as the spirochaetes may wriggle through.

(c) The Volume of Filtrate should not be more than a few cubic centimetres. There are always a few "pores" in the membrane which are considerably larger than the "average pore-size," and the greater the amount of filtrate the more chance there is of a stray particle getting through.

(d) Filtration Pressure is very important. Preliminary tests will indicate what pressure each grade of membrane will withstand (Elford[28]). Always work well within this limit, usually not employing pressures higher than a few centimeters of mercury. Zinsser and Tang's[81] method of noting the permeability to water both *before* and *after* the actual filtration affords a good and simple method of testing the integrity of the membrane.

The Results

Elford[30] has perfected his membranes to a sufficient extent to be able to rely upon their estimated "pore-size" as an index of the size of particles filtering through. Most other results, however, depend upon comparisons with colloidal solutions of known particle size. Now that the methods of determining such particle sizes have been greatly improved, these "standards" would appear to offer a real value if full attention is given to the electrical charge and other adsorption factors when the actual comparisons are made. The complete fulfillment of all the experimental controls we have outlined as an ideal which, although practicable, has not been realized, albeit one or two workers[30,68] have come very near to it. The appended text-figure shows the agreement between the results of a number of authors quoted either because of the excellence of their technique or because of the historical sequence. Additional references are to be found in the bibliography. The data point to a *range* of particle sizes between 20 mμ and 100+ mμ, with the "granules" of the organism of bovine pleuro-pneumonia at the upper end, and bacteriophage at the lower. Some observers think that bacteriophage is even smaller than 20 mμ. Krueger,[52] in particular, finds that his "purified" 'phage passes through 4.5–5.0% membranes, (as compared with 1.5–3.0% membranes which are the usual limit for 'phage and viruses). He estimates its size at about 5 millimicra.

Some of the data in the literature may be too low because of "leaky" filters. Other figures are too high because the particles are not sufficiently freed from gross impurities. Adsorption to cellular debris is the probable explanation of the non-filterability of such viruses as rabies, vaccinia, chicken-pox, and herpetic encephalitis. It is not always a mere question of size.

Sedimentation Experiments

Apart from the concentration of adsorbed viruses (like vaccinia) by centrifugation at, say, 6000–9000 r.p.m.,[19] the ordinary speeds of centrifugation employed in the bacteriological laboratory are inadequate to alter the distribution of viruses or bacteriophage in "filtered" suspensions. The only positive results from sedimentation experiments are those of d'Herelle,[38] who found that a bacteriophage for a *Dysentery Bacillus*, when allowed to stand for 11 months, became ten times more concentrated in the bottom layers than on top. Using a Jouan centrifuge at 12,000 r.p.m. for half an hour, he found that a suspension containing at the outset some 1750 millions per cc of 'phage "corpuscles"(v. supra), resolved itself into an uppermost layer of 50 millions and a lowermost layer of 3700 millions per cc. He was unable completely to free the upper layers of 'phage corpuscles, and his results have not been confirmed.

The Size of Genes

It is the triumph of modern genetics to have adduced powerful evidence to show that the hereditary transmission of units of physical character is bound up with the behaviour of microscopically visible cell structures, especially the *Chromosomes*[75] into which the nuclear chromatin condenses during cell division. It has been found from breeding experiments that character units do not distribute themselves merely by "free assortment," as the original conception of Mendel[59] (1865) presupposed. Bateson and Punnett[7] (1906) showed, in the sweet pea, that characters tend to remain together, "linked" into a number of distinct groups. The fruit-fly (or vinegar fly), *Drosophila Melanogaster*, has proved a remarkably valuable object for breeding experiments. Morgan and his co-workers[20,65,74] examined some 20,000,000 of these flies, all with carefully noted pedigrees. They discovered some 400 "mutants," *i.e.*, new types of individuals with one or more altered genetic or hereditarily transmissible characters. These characters can be paired off into alternatives or "allelomorphs." They fall into just four *linkage groups*, and it is highly significant that each cell of Drosophila during its division contains four pairs of chromosomes, that is, four of maternal and four of paternal origin. In the mature germ and sperm cells, by a process of "reduction division," the chromosomes are reduced to four in number—the halved or *haploid* number. By observations on specimens which chance to have one of the chromosomes missing, it is easy to determine which chromosomes correspond to each linkage group. The group of characters associated with the sex chromosome is an especially profitable field of study. This linkage group contains some 150 characters in Drosophila melanogaster.

To the rule of "linkage" there is an important exception termed *crossing-over.*[74] Thus, in mating a yellow-wing + white-eye female fruit fly to a "wild-type" male with gray-wings + red-eyes, all the daughters are found to have gray-wings + red-eyes, and all the sons have yellow-wings + white-eyes. If these are inbred, 98.5% of the offspring (F_2) are like the grandparents, *i.e.*, they have either yellow-wings + white-eyes or gray-wings + red-eyes. We have, therefore, two "allelomorphic (alternative) linkage groups, yellow-wing + white-eye and gray-wing + red-eye. However, 1.5% of the offspring of the second (F_2) generation have either yellow-wings + red-eyes or gray-wings + white-eyes. In these the linked characters are said to have "crossed-over." Crossing-over usually takes place in "blocks" because the character-units tend to stick together. The frequency with which a character tends to cross-over was shown by Sturtevant[74] to give an index of its closeness to other characters in the same linkage group with which the frequencies can be compared. Each "genetic unit" may be considered to have a definite "locus" on its chromosome, and the different "loci" form a linear chain for which a *map* may be constructed from frequency-of-crossing-over data. The least frequent crossing-over represents the nearest thing to the ultimate genetic unit now known as the *Gene*[63]—and is provisionally estimated (Muller,[65] Morgan[61]), as one-fifth of Sturtevant's "genetic units," but it may be considerably smaller than this. Assuming that the "genes" are of equal size and evenly distributed along the "gene-string" (or chromosome), tentative and rather crude computations of the upper limit of their size may be made, in several ways, as suggested by Morgan in his Croonian lecture of 1922.[61]

By computing, from fixed and stained sections, the average volume of the head of the spermatozoön of Drosophila melanogaster, Morgan presumed that this might be taken as a very rough approximation to the total volume of the 4 chromosomes (haploid number) it contained. Crossing-over data suggested 5 × the known number of genetic units as a conservative estimate of the total number of genes present. It is justifiable to assert from these data that the genes (if assumed to be evenly distributed) are not larger than 77 $m\mu$ in diameter.

The chromosomes, when measured at the "metaphase" of mitotic-division, have fairly uniform width of about 0.2μ and respective lengths of 1.8μ (I), 2.5μ (II), 3.0μ (III), 0.2μ (IV), totalling 7.5μ in all. Their (cylindrical) volume is therefore 0.236μ^3. Dividing by the number of genes (2000, v. supra), and computing the gene diameter, we get a value of 60 mμ.

A still simpler method is to assume that the fully stretched-out chromosome of the "thin-thread stage" of conjugation during cell-division has all its component genes arranged end-to-end. In the case of Chromosome II, this chromosome length may be taken as 11μ. Some 110 genetic units are known to be associated with this chromosome, and we may take 5 × this number as an estimate of the number of genes. If each gene takes up an equal fraction of the "gene-string" the width should occupy about 20 mμ.

A figure of 65 mμ is obtained if the chromosome volume is used, the data being given in the second method.*

Many of the assumptions involved in the foregoing calculations are unwarranted, but the error is always on the upper side. A diameter of 20–80 mμ may, therefore, be accepted as a limiting value definitely above the *gene* size. How far below this limit the gene may be still remains for future elucidation.

More recent cytological data have accrued from measurements of the *chromomeres*, or chromatin aggregates into which the chromosomes of some species are definitely subdivided. Belling[15] has recently photographed the tiny chromomeres of the *Lily*. They average 0.5–0.1μ (or less) across. At the limits of microscopic visibility, with unusually powerful instruments, he discerns a single central dot in each chromosome. This dot is probably less than 0.1μ in diameter. The possibility that this "central dot" is the "locus" if a single gene is a possibility, but is rendered unlikely by data (from other species) which indicate a much smaller number of chromomeres than of hereditary units.

Conclusion

Our data concerning the size of the biological units which we have considered are peculiarly difficult to weave into a definite conclusion. On the whole, they are somewhat too large to reconcile with physico-chemical data concerning the size of the largest known (or suspected) molecules. The lowest estimates of bacteriophage size (5 mμ) are close to Svedberg's[76] values for the haemoglobin molecule. An average figure of 50 mμ in diameter for our biological entities means a volume of a thousand times as great, with room for many hundreds of molecules the size of proteins. The conception of a self-perpetuating catalyst of molecular (? protein) size is an alluring prospect to the materialist in search of the "*Protyle*" of life. Speculation is fruitless, however, until such entities are definitely established by physico-chemical data on the one hand, while the biologist from his viewpoint recognizes their "vital" powers of reproduction, assimilation, and adaptation. It is perhaps insufficiently stressed that genetic phenomena (viewed in their evolutionary significance) are criteria of the "living" which diverge considerably from the

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*Author's calculation.

sequence of inorganic changes. Life still is a great mystery, and in the creed of the biologist its essence is that peculiar "integrative force" which still defies analysis. For the biologist, Biology, and not materialism, must yet remain *the* "working hypothesis."

Estimation of Particle Size of Biological Units

Authority	Date	Biological Agent	Estimated Size	Compared with:	Method
Barnard	1925	Virus of Bovine Pleuro-Pneumonia (a) spheroids (b) granules	 200–250 mμ 150–200 mμ	Bacteria: Supposed viruses of Chicken sarcoma Mouse sarcoma (75 mμ) Human carcinoma	Ultraviolet Photomicrography
v. Angerer	1924	Bacteriophage for B. Dysenteriae	30 mμ	B. dysenteriae	Nephelometry
Bechhold & Villa	1925	Bacteriophage for B. Coli	35–200 mμ	Serum proteins	Gold impregnation
Andriewski	1914	Virus of Chicken Plague	30 mμ	Haemoglobin Serum albumin	Ultrafiltration (collodion)
Duggar & Karrer	1921	Virus of Tobacco Mosaic Disease	30 mμ	Haemoglobin Milk protein Gelatin	Ultrafiltration (various)
Elford	1929 1931	Virus of Bovine Pleuro-Pneumonia (a) spheroids (b) granules Bacteriophage for B. Coli	 200–250 mμ 125–150 mμ 100 mμ	 Red blood cells Bacteria Proteins	Ultrafiltration (collodion)

Authority	Date	Biological Agent	Estimated Size	Compared with:	Method
Olitzky & Boëz	1927	Virus of Foot and Mouth Disease	20–100 mμ	Arsenic trisulphide (100 mμ) Collargol (20 mμ) Haemoglobin (30 mμ) Blue litmus (1.8 mμ)	Ultrafiltration (collodion)
Zinsser & Tang	1927	Bacteriophage for Staphylococcus Rous chicken sarcoma virus Herpes virus	20–100 mμ	Arsenic trisulphide Collargol Egg albumin Casein Trypsin (impure)	Ultrafiltration (collodion)
Prausnitz	1922	Bacteriophage for B. Dysenteriae	20 mμ	Collargol Haemoglobin Gelatine	Ultrafiltration (Haën)
d'Herelle	1918	Bacteriophage	20–30 mμ	Serum globulin	Ultrafiltration (collodion)

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Footnote

General works containing many references are asterisked thus *.

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THE PHYSICAL STRUCTURE OF ELASTIC COLLOIDS

BY W. F. BUSSE

Introduction

Gelatine, rubber, polystyrene, polyesters, soap, chloroprene, etc., differ widely in chemical properties, but they have one outstanding physical property in common—under the proper condition their limits of elastic deformation are enormously higher than those of any similarly shaped crystalline material. Efforts to discover by chemical methods the cause of this high elasticity have not been particularly successful, though they have shown that linear polymers of sufficiently great molecular weights are often highly elastic. The attempts to find a physical explanation of the elasticity in some cases have been partially successful, but no thoroughly satisfactory theory is available.[1-9] The physical theories which have been proposed range from one which assumes the presence of tiny gas bubbles in the material to others which postulate a two-phase brushwork structure, or which assume the existence of helical molecules that act as tiny springs. Although some of these physical theories are satisfactory in limited fields, they usually are not valid for any wide range of materials, and difficulties are often encountered in applying them to a new field. This is illustrated by the attempt to account for the elasticity of rubber on the basis of the two-phase theory of the structure of gelatine gels.[8]

In this paper the mechanics of the process of elastic deformation is analyzed in the attempt to discover the fundamental general conditions which are necessary and sufficient to produce a high degree of elasticity in any material, and to formulate these factors as precisely as possible. The result is an explanation which appears to be more general and comprehensive than previous theories. It is shown that the factors which explain the high elasticity (*i.e.*, the great extensibility and recovery) will also account for other properties such as swelling in solvents, hysteresis, elastic after-effects, etc., which often accompany high elasticity. While specific chemical properties of individual systems are not considered in this analysis, the theory of the physical factors responsible for elasticity is quite helpful in suggesting physico-chemical methods of modifying the properties of various elastic systems. One result of this study has been the production of fibrous and cellophane-like rubbers with rather unusual properties.

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Concepts included in the Term Molecule

In considering the structure of elastic colloidal materials, the gross physical properties are usually explained in terms of the properties of the primary units, or molecules. This, however, leads to confusion unless the various concepts included in the term molecule are clearly differentiated. An analysis of this term along the lines indicated by Bridgman[10] would be of great help in this field, and it is to be hoped that someone will carry it out.

For purposes of this discussion at least three concepts or three types of units which are more or less vaguely included in the term molecule are recognized. The first is the chemical molecule, which is defined as the smallest unit possessing the chemical properties exhibited by a large mass of the material. In this sense the chemist requires the molecules of acetylene, benzene, acetic acid and salt to be written C_2H_2, C_6H_6, CH_3COOH, and NaCl, respectively. These formulas are usually consistent with the common ideas of valence; organic chemists, therefore, sometimes define a molecule as a group of atoms held together by primary valence bonds. Under this latter definition, however, any perfect diamond must be regarded as a carbon molecule, and the so-called molecular compounds are excluded. For practical purposes—*i.e.*, for writing equations—the chemical molecules of solid elements such as iron, sodium, carbon, etc. are considered as single atoms, and the molecules of solid compounds are the smallest groups of atoms that possess the observed ratios of the elements in them, making the copper sulfate molecule $CuSO_4 \cdot 5H_2O$, the iron carbide molecule Fe_3C, etc.

A second concept included in the word molecule may be called the physical molecule. This unit will acquire from thermal vibrations an average of $1/2$ kT ergs of energy for each of three translational degrees of freedom, neglecting quantum restrictions. It is sometimes identical with the chemical molecule, especially in the gaseous state, and the chemist uses this concept of a molecule when he writes the molecules of common gases as H_2, N_2, O_2, Cl_2 and when he uses the weight, in grams, of 22.4 liters of a material in the gaseous state under standard conditions as the gram molecular weight. However, physical molecules also include such units as H, He_2^+, CH_3, which, though not very stable, can be recognized from band spectra; the particles of gold or mastic in colloidal solutions are also good examples of physical molecules. The sizes and weights of the physical molecules of a substance may change with temperature, rate of shear, and other factors, thus differing from the chemical molecules which, by definition, are invariants for a given substance.

When molecular weights are determined by cryoscopic or ebullioscopic methods it is the average weight of the physical molecules which is obtained. When this weight is not consistent with the chemical formulas, special assumptions such as association, ionization or solvation are made to explain the results without always recognizing that several different concepts of molecules are involved. In general, the molecule of the organic chemist is both the physical and the chemical molecule, and cryoscopic methods may, therefore, be used to

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[10] "Logic of Modern Physics" (1927).

determine chemical molecular weights. If there is a discrepancy between the chemical and physical molecules, however, as in the case of acetic acid in a benzene solution, the organic chemist considers only the chemical molecules.

The distinction between physical and chemical molecules has been emphasized before, but the use of these concepts interchangeably still causes confusion in our thinking and discussions. This is particularly apparent in the field of colloids where the distinction between the two concepts is more important as well as more difficult to make, and because a third concept has crept into use which should be distinguished from the first two. When Einstein's equation is used to determine molecular weights by viscosity methods a third concept is introduced into the term molecule and in some cases a new unit is measured. This is a mechanical unit, the group of atoms which hold together when the material is subject to a shearing stress. To show its relation to the other units and to emphasize the broadness of the accepted usage of the term molecule, this unit will be called a "mechanical molecule."

The value of this concept is brought out in the case of compounds which form normal solutions in one solvent while in another they form gels even at very low concentrations. Viscosity measurements of these solutions do not reveal much about the chemical molecules, though they may indicate the size of the mechanical molecules.

In gases and possibly in most liquids the physical and the mechanical molecules are identical; in liquids such as mercury, some of the mechanical molecules probably are also chemical molecules. In solids and in some colloidal solutions, where structures are built up through association forces, the physical and mechanical molecules may be quite different. When the units become very large, as in a macroscopic crystal or piece of a gel, the concept of the physical molecule becomes relatively unimportant, since the kinetic energy of translation acquired from thermal vibrations by a large particle plays only a small part in determining its properties. However, the larger the size of the units which hold together under a shearing force, the more important they are in determining the mechanical properties of a system. It is possible that in some cases the difference between the physical and mechanical molecule in a solid is merely a difference in point of view, but in other cases there seems to be a clear-cut physical distinction. In thixotropic systems such as vanadium pentoxide gels for example, the physical molecules of vanadium pentoxide may contain very large numbers of V_2O_5 particles. At very small shearing stresses the mechanical molecules may also be large groups of V_2O_5 particles, but at large shearing stresses the mechanical molecules may be the single V_2O_5 particles or micelles. The single water molecules, H_2O, as well as the polymers and perhaps the cybotactic groups[11] $(H_2O)_n$ are also mechanical molecules, the proportions of the different groups perhaps varying with temperature, rate of shear, etc.

The size of the mechanical molecule thus is not an invariant, as it changes not only with temperature, rate of shear, etc., but also, particularly in thixo-

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[11] Stewart: Rev. Modern Phys., 2, 116 (1930).

tropic systems, with the time of standing at rest. This is a part of the strength as well as the weakness of the concept; for, since it applies to a unit which can vary as conditions change, its use is not limited to infinitely dilute solutions or gases. The concept applies, for example, to gelatine or rubber solutions or from the most dilute (where the units of the solute which hold together during shear may be chemical molecules) to concentrated gels where association, thixotropy, etc., play important parts; it also applies to solids where the units held together by secondary forces may be more important than those held together by the primary valence forces.

The use of the concept of mechanical molecules makes it possible to avoid, for the time being, the problem of distinguishing between chemical molecules and micelles in dilute solutions, since from the standpoint of the mechanics of flow such a distinction is unnecessary. Likewise, the use of this concept clarifies other problems concerning the structure of solids, such as the question, "Is vulcanization a chemical or physical reaction?", by pointing out that it is the structure of the mechanical units which is important, whether these units are formed by physical or chemical means. It should be emphasized that our concepts are bound up with our methods of measurement and the concepts have value only when they are useful. In this paper the term molecule will be understood to be the mechanical molecule, except when it is specifically stated otherwise, since in most cases the chief interest is in the mechanical properties of the systems.

Ultimately there will probably be a quantum mechanics theory of molecular structure[12,13,14] which will make the above divisions obsolete. However, until then, when these limited concepts must be used, there should be an awareness of their defects as well as of their advantages.

The Structure of Elastic Colloids

The outstanding properties which must be explained by any satisfactory theory of the structure of elastic colloids are:

1. High elasticity—*i.e.*, large deformations which are followed by recovery to substantially the original size and shape upon removal of the deforming force.
2. Storing up free energy on deformation and the return of a large part of it as external work during the recovery.
3. Hysteresis.
4. Elastic after-effect, or slow recovery long (even days) after the deforming force is removed.
5. Swelling in suitable liquids, and sometimes dissolving to give solutions of high viscosity.

In addition, the theory should not be inconsistent with such specific properties as the Joule heat, X-ray fiber diagrams, etc. It should also account for the fact that many gels are elastic, though not all elastic bodies are gels.

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[12] Heitler: Z. Physik, 31, 185 (1930).

[13] Mulliken: Chem. Rev., 9, 347 (1931); Rev. Modern Phys., 4, 1 (1932).

[14] Pauling: Chem. Rev., 5, 173 (1928).

The fact that elastic colloids can be deformed several hundred percent and then recover to their original shape implies the existence of structural units in the material which also have this property. The unit cannot be the atom, for work on the strength of crystals[15] and metals,[16] on band spectra,[13] and on the Raman effect[17] has shown that a very great force is required to increase the distance between adjacent atoms in a molecule or crystal by as much as 30%, and rupture or plastic flow occurs at relatively low elongations. To make possible the elongations observed in elastic colloids, it is essential, then, to have some unit of mechanical structure made of groups of atoms to magnify the limited deformability of the single atoms. Many such structures have been proposed, but in most cases the authors have suggested molecular arrangements which are not common to all elastic colloids (helical rubber molecules, for example) or they have not clearly recognized the essential factors required to produce elastic structures (two-phase gel theories). An analysis of deformation processes indicates that the property of high elasticity requires, and is produced by, the following factors:

1. Groups of atoms which form strong, somewhat flexible fibrous units. These mechanical molecules may be physical or chemical molecules as well.
2. Weak or uniform cohesive (secondary valence) forces around the fibers.
3. An interlocking of the fibers at a few places along their length to form a three-dimensional network. This interlocking of the fibers may occur through chemical combination, by secondary valence forces, or by mechanical entanglements.
4. A means of storing up free energy in the fibers during deformation.

Evidence for the existence and importance of these conditions in elastic colloids will be given, and then it will be shown how these criteria of the necessary and sufficient conditions for high elasticity help to correlate and explain some of the specific physical properties of rubber.

1. *Long Fibers.* The existence of a fibrous brushwork structure in two-phase gels is generally recognized. Such an arrangement is necessary to account for the fact that gels may be obtained containing only a few tenths of a percent dry solid,[18] and that the rate of diffusion of molecules or ions through a gel differs only slightly from that in a sol of the same concentration.[21]

Usher and co-workers[19,20] found that during the gelation of a gamboge sol one could actually observe the particles line up into filaments which form a three-dimensional network, and they inferred that a similar structure existed in gels of cadmium sulfide and other lyophobic materials. They also found that the viscosity of gas black and starch suspensions varied with the pressure only when there was a flocculated structure that could easily be broken up by small shearing forces. By means of a non-uniform dark field illumination,

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[15] Joffé: "Physics of Crystals" (1928).

[16] Mehl: J. Am. Chem. Soc., **52**, 534 (1930).

[17] Andrews: Phys. Rev., (2) **35**, 662 (1930).

[18] Holmes and Maxson: Colloid Symposium Monograph, **5**, 287 (1928).

[19] Usher: Proc. Roy. Soc., **125A**, 143 (1929).

[20] McDowell and Usher: Proc. Roy. Soc., **131A**, 409 (1931).

[21] Reference 9, p. 727.

Szegvari[22] showed that the ultramicroscopic particles of V_2O_5 formed filament or needle shaped groups when the V_2O_5 sols set to a gel, and recent work on the dielectric constants of thixotropic systems indicates that the filament formation during gelation is due to the contact and adhesion of the solid particles to each other, rather than to any immobilizing of the surrounding liquid.[23]

Even in lyophilic gels, much of the liquid is mechanically entrapped in the interstices of some open structure rather than being bound by a chemical solvation, for one liquid in a gel can often be replaced by another of markedly different chemical properties without greatly changing its physical properties. The water in a gelatine gel, for example, may be replaced by organic liquids, or in some cases even by air.[24,25]

X-rays have shown that elastic materials which are not two-phase systems also contain fibrous units. Crude and vulcanized rubbers show an x-ray fiber diagram when stretched,[26] as do stretched dried gelatine[27] and synthetic linear high polymers, provided their molecular weights are great enough.[3,4,28,29] Solutions of these materials have high viscosities and show streaming double refraction.[30] For reasons discussed below a swelling agent must be used with some of these compounds to obtain high elasticity at ordinary temperatures.

While some sort of a fibrous mechanical structure is essential for high elasticity, the shape, stiffness, kinkiness, etc., of the fibers may vary widely among different systems. Nothing very definite is known about the precise shape of the fibers, other than that in materials like rubber, metastyrene, etc., the fibers are relatively thin and flexible—perhaps being only a single chemical molecule thick at most places—while in a fresh silica gel or a gamboge gel the fibers probably are many molecules thick and relatively stiff.

Purely geometrical considerations show, however, that the molecules of rubber do not have a helical shape, as has recently been proposed.[31,32] If the fibers are twisted so that consecutive double bonds are adjacent to each other across one turn of the helix the maximum elongation possible is about 300% or only about one-fourth that actually found in rubber. To make possible the observed elongations, they would have to be in the form of helixes containing 16 atoms of 4 double bonds to a turn. Such a shape would not be stable, however, due to the tendency of large ring compounds to assume irregular forms and to flatten out so that the opposite sides of the ring are adjacent to each other.[33]

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[22] Szegvari: Z. Physik, **21**, 348 (1924).

[23] Kistler: J. Phys. Chem., **35**, 815 (1931); Kallman and Kreidl: Z. physik. Chem., A **159**, 322 (1932).

[24] Kistler: J. Phys. Chem., **36**, 52 (1932).

[25] Erbring: Kolloid-Z., **57**, 195 (1931).

[26] Meyer and Mark: Ber., **61**, 1939 (1928).

[27] Katz and Gerngross: Naturwissenschaften, **13**, 900 (1925); Gerngross and Katz: Kolloid-Z., **39**, 181 (1926).

[28] Carothers, Williams, Collins, and Kirby: J. Am. Chem. Soc., **53**, 4203 (1931).

[29] Carothers and Hill: J. Am. Chem. Soc., **54**, 1566, 1579 (1932).

[30] Signer: Z. physik. Chem., **A150**, 257 (1930).

[31] Kirchof: Kautschuk, **6**, 31 (1930).

[32] Fikentscher and Mark: Kautschuk, **6**, 2 (1930).

[33] Reference 3, p. 378.

Staudinger's assumption that in dilute solution the molecules of linear high polymers are practically straight stiff elastic fibers does not seem reasonable in view of the possibility of rotation around single valence bonds, and this assumption is not necessary to explain his viscosity results. The most plausible hypothesis of the form of the rubber molecules in solution is that they are kinky fibers having a considerable range of lengths which mechanically entrap and practically immobilize a large volume of solvent.[34] This hypothesis is consistent with viscosity experiments carried on in this laboratory,[35] and with the collision areas of straight chain hydrocarbons calculated from the viscosity of their vapors.[36]

2. *Weak Cohesive or Secondary Valence Forces.* Long fibrous units alone are not enough to produce elasticity. Parts of the fibers must be able to slide past each other without great difficulty if there are to be large deformations and recoveries. This implies weak or very uniform secondary valence forces around the greater part of each fiber, as well as implying a flexibility in the fibers themselves.

The weak secondary valence forces may be due to the arrangement of the atoms and so may be a property inherent in the fibers themselves, as is probably the case in rubber. In other cases the fibers have relatively strong cohesive forces, but these can be effectively weakened or insulated by combining the fibers with small molecules which have much weaker secondary valence forces—in other words by swelling the fibrous material with a liquid having a low viscosity. Numerous examples of producing elasticity by this method are known—swelling gelatine with water or glycerine, cellulose esters with dibutylphthalate, metastyrene with styrene, etc. In fact, this method of producing elasticity is so common that it has sometimes incorrectly been assumed that a two-phase gel structure was necessary for high elasticity.[8] It is not two phases that are necessary, however, but rather forces of two different orders of magnitude, strong forces along the fiber and weak forces around the fiber.

Another way of reducing the magnitude of the secondary valence forces is to increase the distance between the molecules by raising the temperature. Metastyrene and rubber hydrochloride are made elastic by this treatment, and cured rubber loses its elasticity when cooled to sufficiently low temperatures.[17] Moreover, Bridgman found that rubber lost its elasticity and was very hard under extreme pressures.

Whitby[4] recognized the importance of weak secondary valence forces when he attributed the slow recovery and what he called "the sub-permanent set" of elastic colloids to a high internal viscosity or an "elastic yield value." However, he states that the cohesive forces responsible for this "elastic yield value" are essentially the same as those responsible for the recovery of the materials after deformation, a view which does not entirely agree with that presented here. Von Weimarn[7] also pointed out that non-uniform "vectorial

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[34] Haller: Kolloid-Z., 56, 17 (1931).

[35] Busse and Karrer: "The Application of Dunn's Viscosity Equation to Rubber Solutions," Atlantic City Meeting of the American Chemical Society, September (1929).

[36] Melavan and Mack: J. Am. Chem. Soc., 54, 888 (1932).

force fields" around molecules made it possible to bring them into a rubbery state, but he also assumed that a helical structure was necessary for elasticity.

3. *An Interlocking of the Fibers at a Few Places along their Length.* The high deformability of elastic bodies is not unique, for liquids and plastics are easily deformed. It is the high recovery of elastic colloids which puts them in a class apart. Shearing stresses can distort and orient long molecules in liquids as well as in solids, as shown by the phenomena of streaming double refraction,[30] etc. However, when the shearing stress is relieved in liquids the molecules quickly slide past each other and assume a random orientation without changing the external shape. In elastic solids the return of the fibers to their normal kinky forms makes the whole sample return to its original shape, showing that there is an interlocking and binding of the fibrous units at a few places along their length which prevents their slipping completely past each other.

The effective strength of the bonds holding the fibers together may vary within wide limits, consequently the range of conditions under which a sample will be elastic, (*i.e.*, will recover almost completely) will be very different for different materials. Some bonds may be weak enough to be broken by relatively small shearing forces as in the thixotropic ferric oxide sols studied by Schalek and Szegvari,[37] the weak gels formed in ammonium oleate solutions, or the flocculated gas black and starch suspensions studied by Usher.[20] In these cases the structure broken by the shearing stresses may again be re-formed on standing. Probably the forces which produce a thixotropic structure are similar to those causing the flocculation of pigments and the formation of crystals.[39]

In other cases the bonds between the fibers are stronger, formed, perhaps, by a mechanical entangling of the fibers, aided by the weak cohesive forces around the fibers. The structure of crude rubber and metastyrene is probably of this type. As one would expect, raising the temperature increases the ease of untangling the fibers, and these materials, therefore, show more slippage, or permanent set, at high temperatures.[38] Reducing the length of the fibers also reduces the chances of the fibers' tangling, and it is found that milling crude rubber, which probably shortens the fibers by an oxidation process[40,41] greatly increases the flow or permanent set when it is subjected to a given force. While unvulcanized, dead-milled rubber flows readily under small forces applied for comparatively long times, it is nearly as elastic as cured rubber if the distorting force is applied for only a short time,[42] *i.e.*, if there is not sufficient time for the thermal vibrations to aid in untangling the molecules.

In vulcanized soft rubber there are much stronger bonds holding the fibers together so that flow and permanent set are small at room temperature, though

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[37] Kolloid-Z., 32, 318 (1923).

[38] Dieterich: Ind. Eng. Chem., 21, 768 (1929).

[39] Jong: Kolloidchem.-Beihefte, 29, 454 (1929).

[40] Cotton: Trans. Inst. Rubber Ind., 6, 487 (1931).

[41] Busse: Ind. Eng. Chem., 24, 140 (1932).

[42] Williams: Ind. Eng. Chem., 21, 872 (1929).

they become appreciable at high temperatures or over long times.[43] This suggests that vulcanization involves a chemical union between different rubber molecules, either through direct carbon to carbon bonds, or by means of sulfur (or Se, O_2, etc.) bridges.

The number of these bonds that exist in soft vulcanized rubber cannot be determined exactly, but some idea may be obtained of the upper and lower limits. The fact that vulcanized rubber can be elongated about 1000 percent of its original length indicates that in this system the interlocking of fibers cannot be more frequent on an average than about one bond for every ten carbon atoms of the chain. This is the upper limit for the number of bonds, and the actual number probably is far less than this. The work of Bruni and Oberto[44] indicates that a minimum of 0.15% sulfur or one atom for each 315 C_5H_8 radicals is necessary for vulcanization, *i.e.*, to produce a noticeable change in the mechanical properties of rubber. Assuming one bond for each sulfur atom, this represents one bond for every 1260 carbon atoms of the chain, which is the extreme lower limit for the number of bonds necessary to affect the stress-strain curve appreciably. If it is assumed that vulcanized rubber is a chemically distinct material, and that two bonds are required for each original chemical molecule, these results indicate a molecular weight of the order of 20,000 for the particular sample of crude rubber which they used. If the theory of elastic deformation presented here is correct, the minimum sulfur required for vulcanization should increase with the amount of mastication of the rubber. One would also expect the amount of combined sulfur required for maximum strength to increase with the amount of mastication and these are found to be the facts.

Blake[45] reports that only 5.2% Se can combine with rubber in the soft rubber cure. If we assume that each Se atom forms a bond between two fibers, there would be a maximum of about one bond for every 23 isoprene groups, or one bond for every 92 carbon atoms in the chain, which, from mechanical considerations, is a reasonable figure.

The necessity for interlocking of the fibers of a gel at a few places along their length was recognized by Kistler,[24] who found that a cellophane aero-gel could be made with a volume 100% greater than the original cellophane, yet with nearly the same strength as the original. In the case of systems made of very flexible fibers such as rubber or gelatine, he could not produce an aero-gel. However, on stiffening the fibers, as on tanning a gelatine gel with formaldehyde, which increased the stiffness of the gel presumably by tying different fibers together with strong bonds, he was able to obtain a gelatine-aero gel.

4. *A Means of storing up Energy during the Distortion of the Fibers.* Since elastic bodies can do work on retraction they must have a means of storing up free energy when they are distorted. This energy may in part be stored as potential energy in the fibers, because of a slight increase in the dis-

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[43] Van Rossem and van der Meyden: Rubber Age, N. Y., **23**, 438 (1928).

[44] Rev. gén. caoutchouc, **8**, No. 75, 19 (1931).

[45] Ind. Eng. Chem., **22**, 744 (1930).

tance between adjacent atoms in the fibers and through a distortion of the valence angles. This idea of a stiffness in the fibers is consistent with the concept of tetrahedral carbon atoms[46] and it also agrees with the new wave mechanics.[47,48] It does not follow, however, that the fibers are even approximately straight rods, or that they have the zig-zag shape attributed to fatty acid molecules closely packed on the surface of water. In long molecules, the thermal vibrations instead of causing the molecules to vibrate as thin glass fibers might easily cause rotation around single valence bonds to produce a very kinky shape. Haller[6] has calculated, on the basis of Raman spectra data for the energy required to deform valence angles, that if the molecules vibrated as rods, the average bending of a paraffin hydrocarbon chain of 100 carbon atoms would be an angle of about 16.4°, while a chain of 10,000 carbon atoms would be bent, on the average, 163.5° from a straight lines. It follows from purely geometrical reasons that thermal vibrations will have a strong tendency to restore a kinky shape to long fibrous molecules after they have been straightened by an external force.[49] Probably at all times there will be a rapid interchange of potential and kinetic energy due to thermal vibrations.

When the fibers are in nearly parallel alignment the effect of thermal vibration in causing contraction may be more than counterbalanced by the tendency of the molecules to form crystalline units with evolution of heat. This is exhibited as racking and as the Joule heat in rubber, and similar effects are observed in chloroprene.[28] Such an effect can be expected only when there is a uniform periodicity in the intensity of the secondary valence forces such as would be obtained when the fibers are made by repeating some simple unit.

If the recovery of elastic colloids is due to the potential energy stored in the distorted atoms and to the effect of thermal vibrations, the elasticity of chemically saturated materials such as gelatine, metastyrene, etc., and of unsaturated ones such as rubber, may be explained on the same basis. It is not necessary then to account for the elasticity of rubber on the basis of the attraction of double bonds across the turns of the helix.[26,50] Nor is this helical structure necessary to account for the S-shape of the stress-strain curve of rubber; for if the stress-strain curve of rubber is calculated on the basis of the instantaneous cross sections of the sample, it is not S-shaped.[51,52]

This stiffness of the fibers also accounts for the swelling pressure of gels. If the fibers are in the normal random kinky shape when a gel such as gelatine is formed in solution, the fibers on drying will be distorted as the gel contracts in size because of the capillary and cohesive forces. After the liquid is evaporated, the cohesion between the separate fibers is great enough to keep them in their distorted positions, in spite of the thermal vibrations which tend to relieve strains at the valence angles. On again putting the gel in water,

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[46] Kettering, Shutts, and Andrews: Phys. Rev., (2) 36, 531 (1930).

[47] Slater: Phys. Rev., (2) 37, 481 (1931).

[48] Pauling: J. Am. Chem. Soc., 54, 988 (1932).

[49] Karrer: Phys. Rev., (2) 39, 857 (1932).

[50] Fikentscher and Mark: Kolloid-Z., 49, 135 (1929).

[51] Hatschek: J. Soc. Chem. Ind., 40, 251 T (1921).

[52] Ariano: India Rubber J., 72, 271 (1926).

the cohesive (or secondary valence) forces around the molecules will be satisfied by the smaller water molecules, and the fibers can then untangle so as to relieve the distortion as much as possible.

The swelling of a gel, then, consists of two parts. The first is an adsorption of the swelling liquid on the gel fibers by means of the secondary valence forces which may involve a liberation of heat. The adsorbed layer effectively insulates these secondary valence forces, thus allowing the fibers to move past each other and assume a random kinky shape with the minimum average distortion of the valence angles. This latter part of the expansion may involve an absorption of heat, even though there is a decrease in free energy.

As the swelling continues new positions of strain may be introduced into the molecules and these may finally balance any further tendency to swell. This limited swelling occurs only when the molecules are long enough to be quite firmly tangled or snarled, or when there is a combination of molecules through very strong forces (polymerization, etc.) to make the sample a mechanical unit, as probably is the case in cured rubber. This effect also appears in gelatine gels which have been formed from solutions of different concentrations. The amount of water they will again take up after drying will be found to depend on the concentration at which the gel was formed, the gels formed from dilute sols taking up more water than gels from concentrated sols.[53] The contacts made at the time the gel is formed determine the amount of swelling that will produce the minimum distortion of the valence angles. The anistropic swelling of gelatine gels observed by Sheppard and McNally[54] also shows that there are strains in the dry gels determined by the conditions under which the gels are formed and dried.

This theory of the cause of the swelling pressure gives a very simple explanation of the results of Stamberger and Blow,[55] who found that a given concentration crude rubber produced the same swelling pressure as dead-milled rubber, though one was a swollen gel and the other a relatively mobile liquid. The effect produced by the tangled molecules trying to expand and minimize the distortion of the valence angles may be visualized as being somewhat similar to the effect produced when a number of tennis balls is placed in a cylinder and compressed by a piston. The balls will exert a given pressure when compressed a definite amount by the piston, and on removing the piston the balls can be poured out of the cylinder. If, however, the balls are coated with an adhesive and then packed into the cylinder in the same way and the adhesive allowed to dry, the balls will be fastened together wherever they come into contact in their undeformed state. The balls will exert the same pressure as before when compressed by the piston, and on removing the piston the group of balls will regain its original shape, but the individual balls cannot be poured out of the cylinder. Similar results would be obtained if the molecules were considered as tangled springs instead of tennis balls. If this picture is correct, and the swelling pressure is independent of molecular size, it

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[53] Reference 9, p. 209.

[54] Sheppard and McNally: Colloid Symposium Monograph, 7, 17 (1929).

[55] Stamberger and Blow: Kautschuk, 6, 22 (1930).

follows that in concentrated solutions, where swelling pressures can be measured, and for compressive stresses, such as are applied in measuring swelling pressures, the volume occupied by the mechanical molecules is proportional to their weight. This relation is very different from the results found by Staudinger[1] and Fikentscher and Mark[50] for dilute solutions, but it is consistent with the view that in solids and concentrated gels the molecules have a more or less compact kinky shape.

Since this paper was presented, a paper by Meyer, von Susich and Valko[70] has appeared in which they abandon the idea of a helical rubber molecule, and conclude that one must avoid the use of models if he is to get a fundamental understanding of the mechanism of elastic deformation. The kinetic theory of elasticity which they present emphasizes the factor of thermal vibrations of groups of atoms within the molecule, and is consistent with the theory given above.

Application of Theory to Specific Properties of Rubber

This theory is of value in interpreting and correlating many of the specific physical properties of elastic systems. In the case of rubber, for example, the theory does not tell anything about the proper accelerators of vulcanization to be used to produce definite properties such as low permanent set, or low hysteresis, or high elongations. However, accepting the view that crude rubber consists of long, kinky, fibrous molecules, and that soft rubber vulcanization produces strong (presumably chemical) bonds between the molecules of crude rubber, one would expect, and actually finds, the following physical properties accompanying those already considered.

1. *Creep and Elastic After-Effect.* Even with relatively weak cohesive forces around the fibers one would expect that any large elongation or recovery would cause the kinky fibers to move so far that some parts would become jammed or tangled up in intermediate equilibrium positions. The energy of thermal vibrations would then cause the jammed groups of atoms, or parts of fibers, to escape slowly from these temporary equilibrium positions and become at least partly untangled. This produces a slow creep after the initial rapid elongation, when the sample is stretched by a constant load. If the rubber is stretched to a constant elongation, this untangling will be manifested as a slow decrease in the stress.

When a stretched sample of rubber retracts, groups of atoms again have to move considerable distances past other rubber molecules, and there is as much chance of these groups jamming in intermediate equilibrium positions as there was during the stretching. These tangles are undone only when the energies of the thermal vibration are great enough to move the groups out of the intermediate equilibrium positions. The resultant continued retraction is the elastic after-effect.

A mathematical treatment of this process is very difficult, and only by making some rather improbable assumptions was it possible to derive rela-

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[70] Meyer, von Susich and Valko: Kolloid-Z., 59, 208 (1932).

tions between length and time which approximately fit the experimental results. Phillips,[56] found that the increase in the length on stretching for vulcanized rubber was given by the formula

$$E = a + b \log t$$

where E is the increase in length, t is the time, a and b are constants. For unvulcanized rubber the formula was of the type

$$\log E = a + b \log t$$

Work in this laboratory has indicated that the latter formula is valid for certain kinds of vulcanized rubber, also.

This explanation of the elastic after-effect, of course, is analogous to the explanation of the slowness of many chemical reactions. A knowledge of the temperature coefficient of this process (measured without complicating side effects) would permit the calculation of the average amount of energy that must be added to a molecule or part of a molecule to remove it from these intermediate equilibrium configurations, or jams, just as a knowledge of the temperature coefficients of chemical reactions makes it possible to calculate the heats of activation.

Elastic after-effects may be produced by the tendency to form fibrous crystals, as well as by the mechanical jamming of the fibers. The racking of crude rubber is an extreme example of this effect. Here the slowness of the retraction is due to time required for the sample to acquire from the outside the heat necessary to melt the crystals, so it might be called a thermal elastic after-effect. Both types of elastic after-effects are reduced by raising the temperature. On lowering the temperature there should be more tangling of the fibers and the rate of disentangling should decrease, due to the greater magnitude of the cohesive forces around the fibers, causing the modulus of rubber to increase as the temperature is lowered, as was found by Mark and Valko[57] and by Rosbaud and Schmid.[58]

It may be mentioned that no elastic after-effect other than that due to thermal, electrical or other secondary thermodynamic effects can occur in a perfect crystal.[59] An elastic after-effect produced by shearing forces requires the existence within the sample of groups of atoms held together by strong forces and surrounded by weak forces.

The mechanism of the jamming of large groups of atoms during deformation and recovery suggested above leads one to expect that rubber will exhibit a higher modulus,—that is, a lower elongation for a given force,—if the force is applied quickly rather than slowly; this actually occurs. Further evidence for the jamming and tangling of the molecules on distortion is found in the experiments of Prache.[60] On loading a sample of crude rubber with a 400-

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[56] Phys. Soc. London, January 29 (1905).

[57] Rev. gén. caoutchouc, 7, No. 64, 11 (1930).

[58] Z. tech. Physik, 9, 98 (1928).

[59] Reference 15, p. 23.

[60] "Le Caoutchouc and Gutta Percha," 15003 (1930).

gram weight he obtained a certain elongation. On reducing the weight to 100 grams the sample contracted to a length less than it would have had if this 100-gram weight had been applied originally. After this contraction the sample then slowly stretched to its normal length under a 100-gram load. The stretching under the 400-gram weight evidently was more rapid than it would have been with a 100-gram load, so there was more jamming of groups in intermediate positions, making the sample stiffer, and causing a larger contraction upon removal of the weight. Rearrangement and untangling of these jammed groups then permitted the sample to further elongate to its normal length when stretched by a 100-gram weight. A similar result was obtained by Mr. Davies of this laboratory by compressing samples of uncured rubber under different weights in the Goodrich plastometer.[61]

3. *Permanent Set.* If the sample does not completely recover from a deformation it is said to have acquired a set. It is important to distinguish between two very different conditions which may produce this effect. The first is a true permanent set, produced when the fibrous molecules are not firmly interlocked. In this case the molecules may relax by sliding completely past each other. This is simply a viscous or plastic flow which reduces the strain in the molecule without changing the external shape of the sample. If this action is carried to the limit the sample becomes isotropic. Anything which will decrease the binding between the fibers, such as raising the temperature, swelling with solvents, etc., will increase the permanent set produced by this cause; reducing the length of the molecules will have the same effect. Milled rubber acquires a greater permanent set than unmilled rubber and the permanent set is lowest for the highest members of a homologous series of polymers.

The second cause of permanent set is essentially a very slow elastic after-effect, usually a thermal elastic after-effect as in racked crude rubber. If the temperature is lowered far enough, cured rubber will show a similar effect, for at the lower temperature the balance between the cohesive forces, thermal vibrations and strains at the valence angles is changed so the molecules no longer can contract. Whitby called this slow elastic after-effect the "sub-permanent set." Raising the temperature or adding solvents to rubber will reduce this type of elastic after-effect.

It follows from this mechanism that not only will the modulus of the rubber increase, but the permanent set will decrease when the speed of deformation increases. The elastic recovery of crude milled rubber is nearly as great as that of cured rubber if the time of deformation is small. This can be demonstrated by bouncing balls made of cured rubber and milled crude rubber. They will bounce to nearly the same height, although they have very different values for stiffness and permanent set when the loads are applied for longer times.[42] In a rapid deformation cycle the mechanical tangling and jamming of the molecules is sufficient to keep them from flowing even though there are no strong chemical bonds holding the fibers together. There is not enough time for thermal vibration to aid in getting the molecules out of the intermediate equilibrium positions or to flow. The sample, therefore, shows a high recovery.

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[61] Karrer, Davies and Dieterich: Ind. Eng. Chem., Anal. Ed., 2, 96 (1930).

4. *Hysteresis.* For a minimum hysteresis in a sample of rubber which is subjected to mechanical distortion, it is necessary to reduce to a minimum the slow creep and elastic after-effects as well as the plastic flow. Such a result would be accomplished if there were a weak binding force or attraction between the molecules permitting them to slide past one another easily everywhere except at the few points where there is the strong interlocking necessary to prevent plastic flow. This condition may be realized if rubber is swollen with a large amount of oil and then vulcanized. The quivering of a cured cement, for example, shows that its hysteresis actually is very low, at least for small deformations.

The hysteresis due to the tangling and untangling of the molecules may be reduced by going through the deformation cycle either very rapidly or very slowly, provided the permanent set is low. In the first case there will be a great deal of tangling. However, since there is little time for the fibers to become untangled the sample will exert nearly the same force during the recovery as it does during the stretching. In the second case, when the rate of stretching and recovery is very slow the thermal vibrations enable the fibers to take up equilibrium positions during both the stretching and recovery, so the hysteresis loop is small if there is no permanent set.

Another method of reducing hysteresis and securing equilibrium stress-strain curves is to help the molecules out of the jams by making the sample oscillate during the stretching. Stress-strain curves of this type were obtained by Gerke.[62] One would expect from thermodynamic considerations that the modulus of the rubber would be somewhat greater at high temperature than at low temperature for the stress-strain curves obtained in this way, and the limited data reported by Gerke indicated that such may be the case. His results also showed that time of cure has no effect on the equilibrium stress-strain curve and he cited this as evidence that the curing of rubber affects the plastic properties of rubber more than the elastic properties; Williams[42] reached a similar conclusion from the study of stress-strain curves at high speeds. It is evident that cure influences the elastic after-effect and creep as well as the plastic flow, and these are parts of the elastic properties of rubber.

This analysis of the deformation of rubber differs considerably from that of Ariano[63] who postulated a "point of viscous diffusion," "plastic state," and "liquid viscous state" between the solid and liquid states to explain the observed elastic properties. As a real explanation of the behavior of rubber under mechanical distortion, the molecular mechanism suggested above seems greatly preferable to naming hypothetical states between idealized solid and liquid states.

5. *Other Physical Properties.* The optical properties sometimes give considerable information about the chemical as well as the physical structure of materials. Recent work on the Raman spectra provides a very convenient method for studying the infra-red absorption spectra of various materials, and it was thought that this line of attack might show something about the struc-

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[62] Ind. Eng. Chem., **22,** 73 (1930).

[63] Nuovo Cimento, March 1929; India Rubber J., **78,** 316 (1929).

ture of rubber and similar hydrocarbons. Preliminary experiments were carried out by Professor Williams and Mr. Hollaender at the University of Wisconsin, to see if the Raman spectra of rubber, gutta-percha and balata in carbon tetrachloride solutions showed any distinctive differences. Since the materials were all carefully purified they darkened readily through oxidation on exposure to air. This made it difficult to obtain the Raman spectra. On exposure to a mercury arc, however, the gutta-percha solution showed a few Raman lines around 4600 Å, probably excited by the mercury line 4359 Å, and a broad band around 4780 Å. Pale crepe and balata showed similar bands. Others have also found broad bands in studying the Raman effect of rubber solutions.[64] The fact that bands rather than lines are obtained may be due to the high viscosity of the solution, or it may indicate that the rubber groups can respond to a wide range of frequencies. It was found in this work that all the solutions gelled on the side exposed to the light, although they were in pyrex glass vessels which transmit only down to a wave-length of 3200Å. This gel structure formed in gutta-percha and balata as well as in rubber. It probably is not identical with that produced by vulcanization with sulfur or sulfur chloride, but at least it involves the linking together, by rather strong bonds, of units which previously were separated.

The tendency of kinky fiber molecules to expand and relieve the internal stresses accounts for the swelling pressure and the mechanical entrapping of liquids by gels, and it also implies that a similar mechanical entrapping of solvent should occur in solutions. Work done in this laboratory[35] several years ago on the temperature coefficient of the viscosity of rubber solutions supports the view that their high viscosity is due to this cause.

Dunn,[65] Andrade[66] and others have shown that the change of viscosity with temperature of non-associated liquids can be represented by an equation of the type $\log 1/\eta = A/T + B$, where η is the viscosity, T the absolute temperature, and A and B are constants. By assuming that the fluidity $(1/\eta)$ is a measure of the rate at which molecules acquire sufficient energy q to leave their transient equilibrium positions (cybotactic state[11]), the writer derived the above relation between fluidity and temperature in the form $1/\eta = CS^{r-1}\,e^{-q/kT}$, where S is the shearing stress, C and r are constants, and the other terms have their usual significance. This equation includes the relation between shear and fluidity found by Nutting. The validity of this interpretation of viscosity is confirmed by data recently published showing the relation of viscosity to the perfection of orientation for 22 octyl alcohols.[67] The changes in the constants C and q, or A and B can, therefore, be interpreted in terms of changes in the structure of the solutions. Tests on rubber solutions in several solvents and over a wide range of temperature and concentrations showed that the value of q in pure solvents differed only slightly from the values in rubber solutions, provided they were not too concentrated.

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[64] Franklin and Laird: Phys. Rev., (2) **36**, 147 (1930).

[65] Trans. Faraday Soc., **22**, 401 (1926).

[66] Nature, **125**, 582 (1930).

[67] Stewart and Edwards: Phys. Rev., (2) **38**, 1575 (1931).

If there were an adsorptive binding of the solvent to the rubber molecules such as was assumed by Fikentscher and Mark,[50] one would not expect this result, so it is probable that the binding of the solvent molecules is largely a mechanical entangling.

6. *Cured Racked Rubber.* Fibrous rubber has been produced in various ways: racked rubber which has been cooled to liquid air temperatures can be shattered to show a fibrous structure; Kirchhof[68] and Mark and Susich[69] obtained fibrous materials by allowing racked rubber to react with sulfuric acid, chlorine, bromine, and iodine at low temperatures for periods up to several months. Mechanically fibrous materials were obtained in every case, but the bromine treated rubber did not give an x-ray fiber diagram. All these materials were relatively weak or brittle and did not have any remarkable physical properties.

From the above theory of rubber structure it was thought that vulcanizing rubber destroys its ability to become racked for one of two reasons. If during vulcanization random bonds are introduced between the fibers this will cause additional strains and distortions when the fibers are arranged parallel to one another by an external force, and the additional strains will prevent the secondary valence forces from holding the fibers in position except at very low temperatures. It is also possible that the chemical reaction during cure changes the intensity and distribution of the secondary valence forces so that the fibers cannot be made parallel, or else the forces are not strong enough to hold them parallel if they are oriented by an external force. In either case one would expect to obtain a rather interesting product if the rubber were first racked and then cured. Attempts to cure racked rubber with sulfur and ultra accelerators at room temperature or slightly above usually resulted in producing what was in effect merely a cured rubber with a strong calender grain.

When racked rubber was cured in a stream of dry sulfur chloride vapor, a strong, horny, fibrous product was obtained with rather unusual properties. It was found that the tensile strength of the samples depended greatly upon the elongation previous to cure, just as the strength of rubber at very low temperatures depends on the elongation of the sample before cooling.[57] In one case sheets of evaporated latex 0.005″ thick were cured in a stream of dry sulfur chloride vapor for 15 min. at 0°C, after being racked different amounts. The tensile strengths varied from about 200 to 17,000 lbs./sq. in., as shown in the following table:

	Tensile Properties of Cured Sample	
Initial Stretch	Ultimate Elongation	Tensile Strength
0%	15%	220 lbs./sq. in.
300	20	4,560
600	20	7,070
900	30	10,450
1200	25	17,100

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[68] Kautschuk, 5, 9 (1929).

[69] Kolloid-Z., 46, 11 (1928).

Similar results have been obtained at room temperature or even higher, over a wide range of curing times. If the samples are very thick only the surface is cured leaving the inside still uncured even after several hours, and the samples are relatively weak and brittle. It is probable that the tensile strengths shown in the above table are not the maximum that can be produced, and it is likely that rubber fibers can be prepared with a strength comparable to the best textile fibers. Samples of cured racked rubber gave sharp x-ray fiber diagrams.

The fibrous product is cured to the hard rubber stage by the sulfur chloride. In one case a 30-minute cure gave a material containing 15.2% sulfur, while the compound $(C_{10}H_{16})_2 S_2Cl_2$ requires 15.7% sulfur. The cured racked rubber may be left in sulfur chloride vapor up to 15 hours without noticeably changing its tensile properties, although the unstretched rubber becomes very brittle when left in the vapor for fifteen minutes.

From the point of view of the mechanical structure of rubber presented here one would expect that fibers could be obtained by stretching cured soft rubber and further curing it in sulfur chloride vapor while stretched. This was tried, using a rubber-sulfur mixture and accelerated stocks, and fibrous rubbers were obtained in every case. However, the accelerators, zinc oxide, age resisters and other compounding ingredients made it necessary to increase the time of cure, and the final product was not quite as good as that obtained with crude unmilled rubber. This may have been because the cured rubber could not be elongated as much as the evaporated latex.

If the rubber is stretched in two directions at once and then cured, a very interesting non-fibrous parchment-like material is obtained. In this case the molecules probably are stretched out into fibers which are oriented at random in a plane. The product is quite strong and flexible in thin sheets, and is very resistant to organic liquids, even boiling toluene does not change it appreciably.

Summary

1. Some of the concepts included in the term "molecule" are briefly discussed and it is pointed out that the mechanical molecule is often the most important one in colloid systems.

2. The elastic properties of colloid systems require, and are produced by a group of four factors:

    (a) Long fibrous molecules.
    (b) Weak or uniform cohesive forces around the fibers.
    (c) An interlocking of the fibers.
    (d) A means of storing up free energy when the fibers are distorted.

3. Evidence for the existence of these factors in elastic colloids is discussed and is applied to account for and correlate some of their physical properties.

4. The theory of the structure of elastic colloids presented here has suggested means of preparing fibrous and parchment-like rubbers having rather unusual properties.

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May 10, 1932.

THE SEPARATION AND IDENTIFICATION OF SOL RUBBER HYDROCARBONS

BY THOMAS MIDGLEY, JR. AND ALBERT L. HENNE

The hydrocarbon occurring in natural rubber is not homogeneous. This has been demonstrated repeatedly by separation into a more soluble portion, called "sol rubber," and a less soluble portion, called "gel rubber."

A variety of methods, all based on solubility difference, have been employed to bring the separation about. The best known are: (1) the slow diffusion of rubber in petroleum ether, a method originated by Caspari[1] and improved by Feuchter[2] and by Pummerer and Miedel,[3] and (2) the separation by means of absolute ether into an "ether-soluble portion" and an "ether-insoluble portion."[4] However, the same methods in the hands of different experimenters have given discordant results, and the conclusions have been debatable. For instance, Hauser[5] found that after a first separation, rubber can be refractioned again into sol and gel rubber and from this he concludes that sol and gel form an equilibrium mixture which will automatically be regained when one of its constituents is decreased or eliminated. Whitby[6] observes that different solvents furnish different ratios of sol/gel, and he concludes that the rubber hydrocarbon is a mixture of molecules of varied sizes.

It appears that the investigators employing diffusion methods, implicitly assumed that sol and gel rubber were not miscible in each other, and that in its essence, the separation was analogous to that of sugar from sand by water.

The apparently incoherent results obtained by diffusion separation are rendered quite reasonable when the mutual solubility of sol and gel is taken into account. A single diffusion of rubber in a given solvent establishes a two phase system, each phase of which contains both sol and gel rubbers, but in different proportions. In other words, diffusion accomplishes only a partial separation.

As a means of coarse separation, diffusion is quite acceptable; but if complete separation is desired, refractionation until the fractions are no longer altered is essential. For this purpose, diffusion is unsatisfactory, because the length of time required to reach equilibrium is sufficient to allow the rubber solution to degrade.

Proponents of the diffusion methods may argue that degradation occurs only in the presence of oxygen, and that a fractionation by repeated diffusion in an inert atmosphere cannot be criticized. This may be true. But it must be borne in mind that given sufficient time, minute quantities of oxygen are

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[1] Caspari: J. Soc. Chem. Ind., 32, 1041 (1913).

[2] Feuchter: Kolloidchem. Beihefte, 20, 434 (1925).

[3] Pummerer and Miedel: Ber., 60, 2148 (1927).

[4] Pummerer: Kautschuk, 1927, 233-6; Pummerer and Pahl: Ber., 60, 2152-63 (1927).

[5] Bary and Hauser: Rev. gén. caoutchouc, 1928, No. 42, 3-11.

[6] Trans. Inst. Rubber Ind., 5, 184-95 (1929); 6, 40-62 (1930).

sufficient to cause considerable degradation, and the complete elimination of oxygen is a difficult experimental accomplishment. Hence, the diffusion method is not practical for refractionation.

A method of fractionation based on precipitation at different temperatures has been described and advocated in a series of previous papers.[7] This method is not subject to the same criticism as the diffusion method, because it establishes equilibrium in a short period of time. The degradation which occurs despite the careful elimination of oxygen during the procedure is so slight that it does not obscure the results nor vitiate their interpretation.

Method of Separation

The temperature differential method is based on the different solubilities of the hydrocarbons of rubber in a certain solvent, at a certain temperature. It makes use of the fact that mixtures of rubber, benzene and alcohol are single-phased within certain limits of concentration and temperature, and, upon cooling, separate into two phases at a definite temperature. One of the phases contains the sol rubber in preponderant quantity, the other contains most of the gel rubber. By repeating the process the preponderant constituent of one of the phases is progressively freed of the principal constituent of the other phase. The experimental details and the efficiency of the procedure are outlined in the appendix.

Criterion of Identification

No fractional procedure of any kind can be satisfactorily performed without a criterion to judge the progress of the fractionation. The measurement of a physical constant such as density, refractive index, melting point, etc., is generally used: in the case of rubber, this is impractical, and consequently a specially standardized physical constant has been devised and called "standard precipitation point," or by abbreviation, "s.p.p."

The standard precipitation point is defined as the temperature at which a slowly cooled mixture of 0.85% of rubber, 28.55% absolute alcohol and 70.60% benzene shows a sudden increase of turbidity. The experimental details needed to measure an s.p.p. are given in the appendix.

Results

The application of the temperature fractionation method, controlled by adequate s.p.p. determinations to a variety of rubber specimens has given the results graphically represented in Figs. 1 to 4. The mode of representation is the same as for an Engler distillation.

In addition to the preceding cases, a sample of smoked sheet was fractioned: the s.p.p. of its sol fraction was found to be 34.8°.

Irrespective of their source, the sol rubbers present the same characteristics, *i.e.*, they are white, translucent, semi-plastic, elastic substances. Tackiness is absent from s.p.p. 33° upwards, but is quite noticeable at s.p.p. 32° or lower. Pure sol rubbers are unstable at room temperature. Degradation is detectable after a few days despite precautions against oxygen. Storage in

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[7] Midgley, Henne and Renoll: J. Am. Chem. Soc., 53, 2733 (1931); 54, 3343, 3381 (1932).

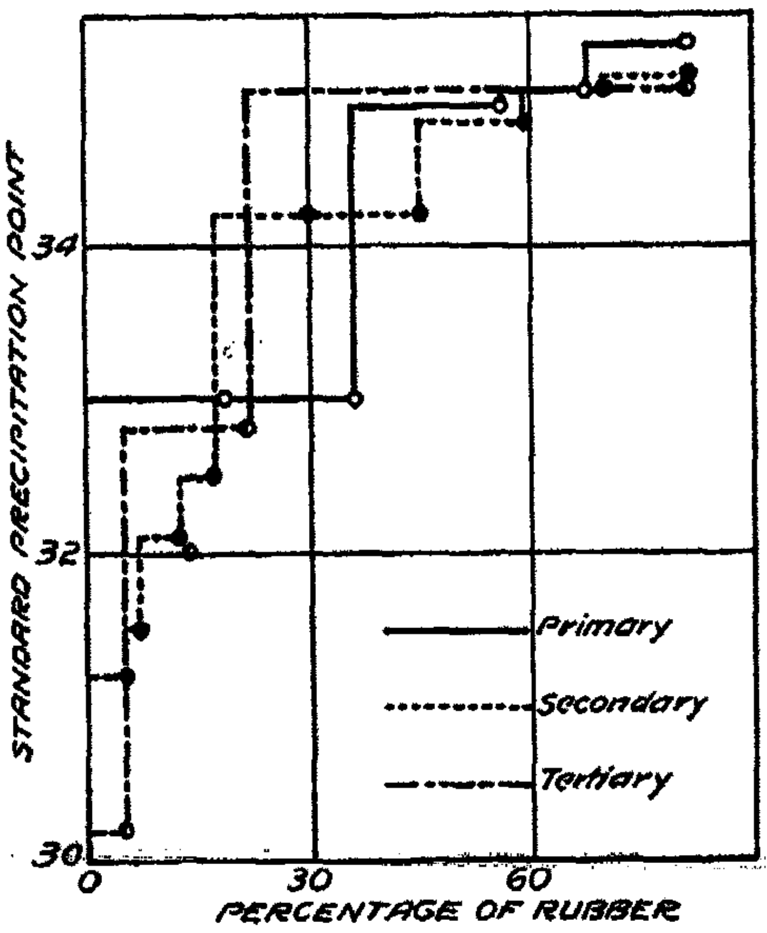

FIG. 1
Fractionation of Crepe Rubber

solid carbon dioxide retards degradation but does not prevent it completely. No tendency to form gel rubber, or equilibrium mixtures thereof has been observed.

Interpretation

A comparison of the results reported in Fig. 1 (pale crepe) and Fig. 2 (milled rubber) shows that extreme milling degrades both sol and gel rubbers. Hence it is reasonable to assume that the presence of components of low s.p.p. in Fig. 1, is due to the sheeting process undergone by the rubber before being

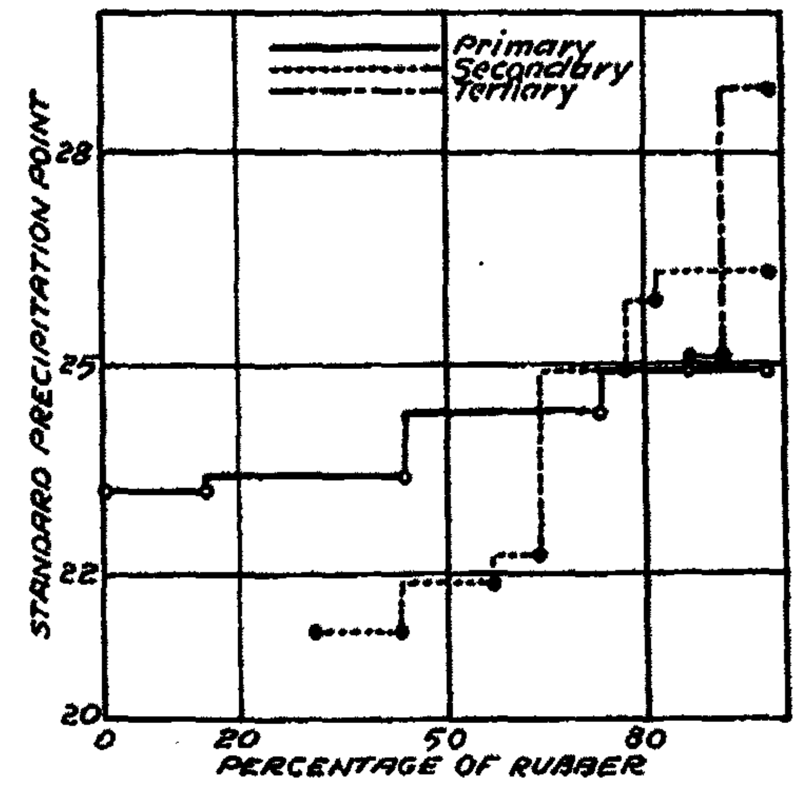

FIG. 2
Fractionation of Milled Rubber

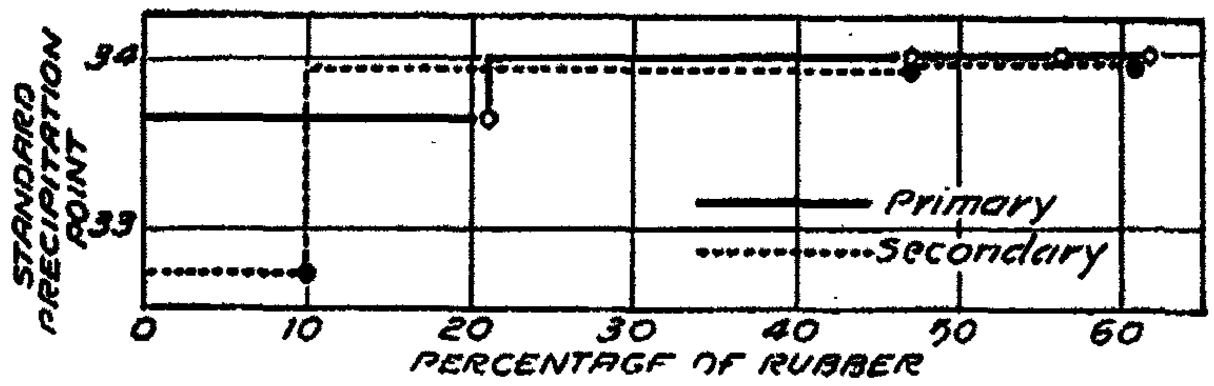

Fig. 3
Fractionation of Spray Rubber

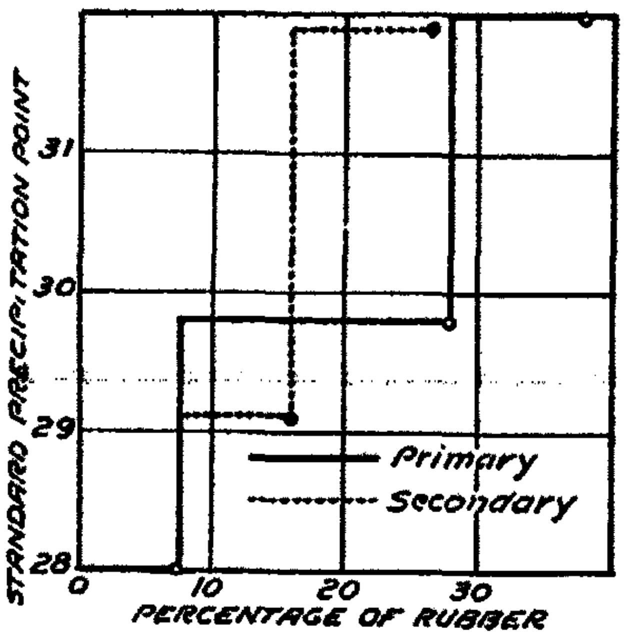

Fig. 4
Fractionation of Guayule Rubber

baled. With this in mind, the results reported in Fig. 3 (sprayed rubber) indicate that nature produces only one sol rubber in a given specimen. This does not mean that natural sol rubber is a single invariable compound; variations occur between sol rubbers of different specimens. The limited number of specimens studied, and their insufficiently known history preclude, at the present time, any conclusion as to the factors involved in this variability. Seasonal, soil, and climatic conditions suggest themselves as suitable for continued research.

Conclusions

(1) Nature produces a definite sol component in any single specimen of natural rubber.

(2) The sol component can be separated and purified by refractionation methods.

(3) Purified sol rubber retains the physical properties of natural rubber; it can be vulcanized to yield a product of superior qualities.

(4) No experimental evidence exists to justify the opinion that rubber is a two-phase system.

(5) Sol rubber and gel rubber are mutually soluble.

Appendix

Determination of the Standard Precipitation Point, s.p.p. A 1.288 g sample of the rubber (free from solvent) is placed in a 250 cc Erlenmeyer flask. One hundred cc of C.P. benzene is added. The flask is set away in the dark, under CO_2, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc of benzene and 56 cc of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees C is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experimental precipitation point. It is reproducible to ±0.1°. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250 cc receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to insure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified CO_2 through the system, the solvents are distilled with a steam bath. The distillate is weighed, and its refractive index is measured in a Pulfrich refractometer, at 20.0°. From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart Fig. 2, paper VII,[7] the experimental precipitation point is then corrected to standard conditions, *viz.* 28.55% alcohol and 0.85% rubber. This is the s.p.p.

Fractionation Procedure. Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% was dissolved in 8083 g of benzene, heated to about 50°. A hot mixture of 4500 cc of absolute alcohol and 1400 cc of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50 cc sample, was 43.0°. The mixture was then held at 42.0° in a thermostat, for one hour. At the end of this period, the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g of rubber hydrocarbon, hereafter designated as A_1. After removal of the A_1 rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of 43.5°. Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g of rubber hydrocarbon was obtained, called A_2 hereafter. Two repetitions of these operations yielded fractions A_3 and A_4.

After the fraction A_4 had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol-benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A_5. Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A_6, while the insoluble matter was called B.

Efficiency of the Procedure. The efficiency of the separation method is illustrated as follows. A 10 g specimen (s.p.p. 35°) and a 10 g specimen (s.p.p. 28.9°) were dissolved in the same batch of benzene and separated by fractional precipitation. A single fractionation yielded 11.5 g of (s.p.p. 34.9°) 8.5 g of (s.p.p. 28.5°).

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THE STRUCTURE OF GELATIN SOLS AND GELS

Part V. The Insolubilization of Gelatin by Heat

BY S. E. SHEPPARD AND R. C. HOUCK*

Insolubilization of gelatin, *i.e.*, loss of capacity to dissolve completely in water at 40°C and above, appears to have been first observed by Hofmeister.[1] He found that gelatin which had been heated to 130°C was not readily soluble in water, in fact could only be brought into solution by boiling for several hours. Bogue[2] found that glue heated at 110°C for 15 hours became insoluble. The change was attributed by Hofmeister to a reversal of conversion of collagen to gelatin which he expressed by the equation

$$\underset{\text{collagen}}{C_{102}H_{149}O_{38}N_{31}} + H_2O \rightleftharpoons \underset{\text{gelatin}}{C_{102}H_{151}O_{39}N_{31}}$$

He regarded collagen as the anhydride of gelatin. There appears to be no definite evidence either for this particular molar ratio of collagen to water as essential for the transformation, nor for a molecular unit of the magnitude 2500 for collagen.

Emmett and Gies[3] disputed Hofmeister's theory of reconversion. They claimed that heated gelatin was digested by trypsin, while collagen was not. They further stated that collagen loses ammonia on conversion to gelatin with boiling water, while the insolubilized gelatin gives up no ammonia on heating with water. This last statement appears to us to be generally incorrect; we have not found any evidence of ammonia being liberated in the conversion of hide collagen to gelatin—provided the collagen had been delimed and neutralized.

The Relation of Gelatin to Collagen

In the first paper of this series[4] dealing with the viscosity of gelatin sols and its change on heating, the following theory of gelatin formation was proposed: "We suppose, in agreement with Meyer and Mark's X-ray investigations that the protein *collagen* consists of fibers built up of crystallites composed of primary valence chains of the anhydro-(peptided) amino-acids—the protein macromolecules. The formation of gelatin consists in the peptization of these fibers, but the primary valence chains become disoriented and separated; complexes of these chains, possibly in a partly oriented or smectic ordering bind water by dipole orientation. On this view, the molecules of gelatin are fundamentally identical with those of collagen, the difference being only in the degree of association and orientation."

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*Communication No. 502 from the Kodak Research Laboratories.

[1] Z. physiol. Chem., 2, 299 (1878).

[2] Chem. Met. Eng., 23, 5 (1920).

[3] J. Biol. Chem., 3, 33 (1907).

[4] Sheppard and Houck: J. Phys. Chem., 34, 273 (1930).

In the second paper[5] Sheppard and McNally stated "the increase in optical anomaly obtained by stretching and drying gelatin jellies represents a movement in the direction of reversing the process:

Collagen ⟶ Gelatin."

It was pointed out that these results were in agreement with those of Katz and Gerngross[6] on the similarity of the X-ray diagrams of collagen and of stretched dried gelatin. We shall discuss the deductions from X-ray spectrography later.

Absorption of Water by Collagen and Gelatin

The absorption of water by gelatin is very much greater than by collagen. The experiments of Sheppard and McNally[7] showed that stretching gelatin jellies before drying decreased the subsequent swelling in water in the direction of the stretch. No considerable change in total water absorption was observed, but the actual elongations effected were not very large. We have produced subsequently very large elongations or distentions of gelatin jellies by the method of Katz and Gerngross (strips of jelly soaked 4-5 days in 60% alcohol-buffer mixture), of the order of 200% along the axis of stretch itself. Birefringence measurements on these showed that a very considerable degree of orientation had been effected.

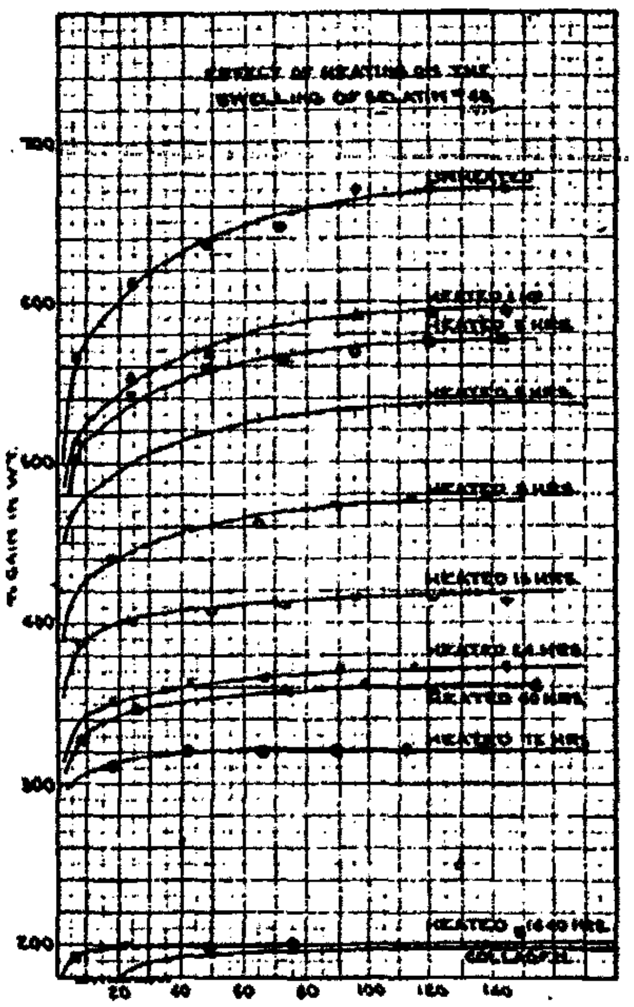

Fig. 1

However, compared with jelly strips of the same concentration identically treated except that they were not stretched and dried under tension, the stretched gelatin did not show any lowering of total water absorption. It appears evident that although the (re-)orientation produced by stretching has assimilated gelatin to collagen in some respects, yet there remains a definite structural difference which allows (a) greater water absorption, and (b) solution in water at 40°C and above.

We have made, therefore, a study of the insolubilization of gelatin by heating at various temperatures.

Experimental

Gelatin strips of Eastman De-Ashed Gelatin No. 48 coated to 0.005″ thick were used. (This gelatin contained 0.5% heat coagulable protein.) The strips

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[5] Sheppard and McNally: Colloid Symposium Monograph, 7, 17 (1930).

[6] Kolloid-Z., 39, 180 (1926).

[7] Loc. cit.

were heated for various increasing lengths of time, and the water absorption at 15°C was measured, the liquid being $M/1000$ acetic acid-sodium acetate buffer at pH 4.95, the isoelectric point of this gelatin. The buffer solution was changed daily, pH being determined electrometrically. The water absorption was determined at different times by weighing, until equilibrium was reached.

The results for heating at 105°-110°C are shown by Tables I-XI and in Fig. 1.

TABLE I

Water Absorption of Gelatin 48
(Heated at 105°-110°C)

Heated for 1 hour		Heated for 2 hours		Heated for 5 hours		Heated for 8 hours	
Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight	Time hours	% Gain in weight
7.3	515	6.2	504	3.2	467	17.7	441
24.5	554	23.5	543	20.6	497	42.2	458
49.0	568	48.1	559	45.2	518	65.2	462
72.1	568	71.1	563	68.2	512	88.7	473
95.6	592	94.6	568	91.7	532	114.2	479
121.1	594	120.1	575	117.2	534	136.9	476
143.8	593	142.8	577	140.0	537		

Heated for 16 hours		Heated for 24 hours		Heated for 40 hours		Heated for 48 hours	
7.9	389	18.3	352	8.4	338	18.9	342
25.1	404	42.9	362	26.3	347	41.9	344
49.7	409	66.7	367	49.4	346	64.4	350
72.6	413	90.2	373	72.9	358	89.9	356
96.2	418	115.7	372	98.3	362	112.6	355
121.7	418	142.5	373	121.1	357	138.1	354
144.5	415			154.7	362	163.1	357

Heated for 72 hours		Heated for 1440 hours	
Time hours	% Gain in weight	Time hours	% Gain in weight
18.0	311	6.1	193
41.5	320	22.5	199
65.9	320	46.8	199
88.7	321	70.1	201
112.1	315	147.6	205
136.0	323	243.4	199

As may be seen, the water absorption values decreased steadily with time of heating, approaching a limiting value after heating 2 months (ca. 1440 hours) of 199%. This value approaches closely that found for the limiting water absorption of collagen (from hide) which gave 200% regain. Reconditioning the heated material by exposure to air of approximately 50% R. H.

for 50 days produced practically no change in the water absorption. Furthermore, gelatin heated more than five hours at 106° to 110°C was incompletely peptized by warm water, the extent and ease of peptization falling off rapidly with further heating.

Order and Heat Increment of the Reaction

As a variable proportional to the concentration (or original gelatin) we have taken the "equilibrium per cent regain" for a sample of gelatin heated for time *t*, minus the "equilibrium per cent regain for infinite time." Calling this $C - C_\infty$, we found for C_∞ the value 200—as stated, the same as for collagen. On graphic analysis of the reaction curves, it was found that plots of $1/(C-200)^2$ against time *t* yielded straight lines in the case of the three gelatins tested (Nos. 48 and 50 Eastman De-Ashed and No. 6432 Commercial). This corresponds to an equation of the form

$$1/x^2 = kt \quad \text{or} \quad dx/dt = k\,(a-x)^3$$

i.e., a termolecular reaction. The results for gelatin No. 48 heated at 107°C are shown in Table II.

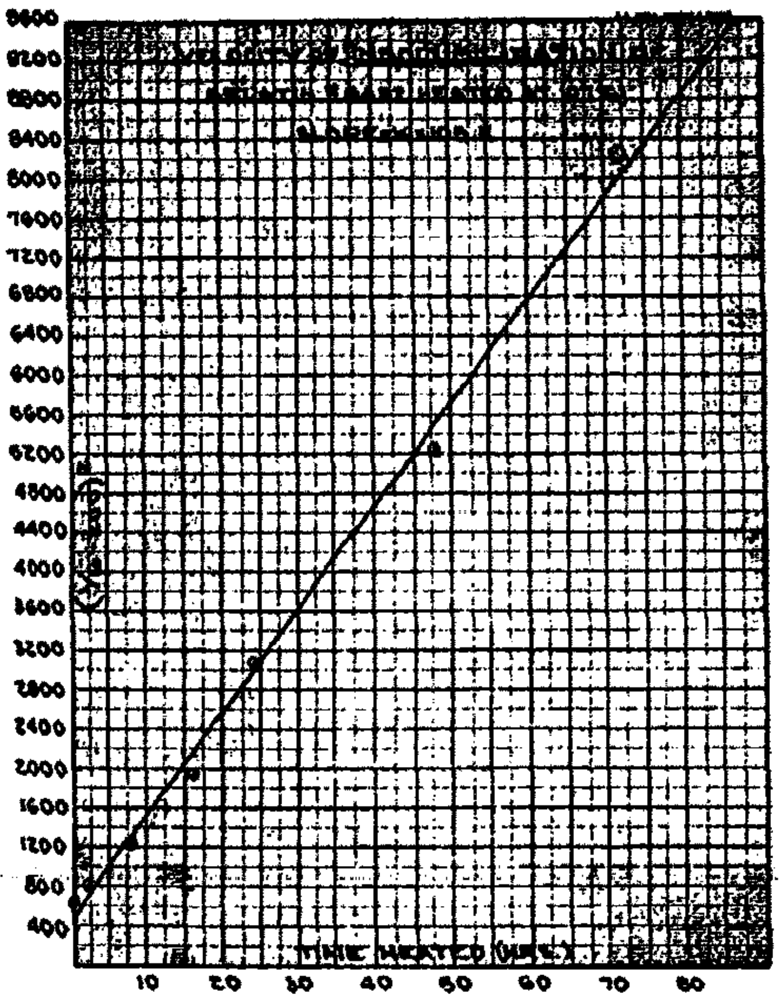
TABLE II

Velocity of Insolubilization by Heat of Gelatin No. 48 at 107°C

Time Heated in hrs.	G % Gain in weight	G-200	1/G-200	1/(G-200)²
0.0	668	468	2.13×10^{-3}	454×10^{-8}
1.0	593	393	2.54	645
2.0	576	376	2.65	702
5.0	537	337	2.96	876
8.0	476	276	3.62	1310
16.0	418	218	4.18	2097
24.0	372	172	5.81	3375
40.0	362	162	6.17	3806
48.0	355	155	6.45	4160
72.0	320	120	8.33	6938
1440	199	0		

To obtain the temperature coefficient of the reaction, the velocity constants were determined for different temperatures, using gelatins No. 50 and No. 6432.

At 60°C the rate of insolubilization was too small to be measured in convenient time, no appreciable change (diminution of swelling) being effected in 48 hours. Results obtained at 90°, 107° and 116°C for gelatin No. 50 are given by Tables III and IV and Figs. 3-7.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6800
6400
6000
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3600
3200
2800
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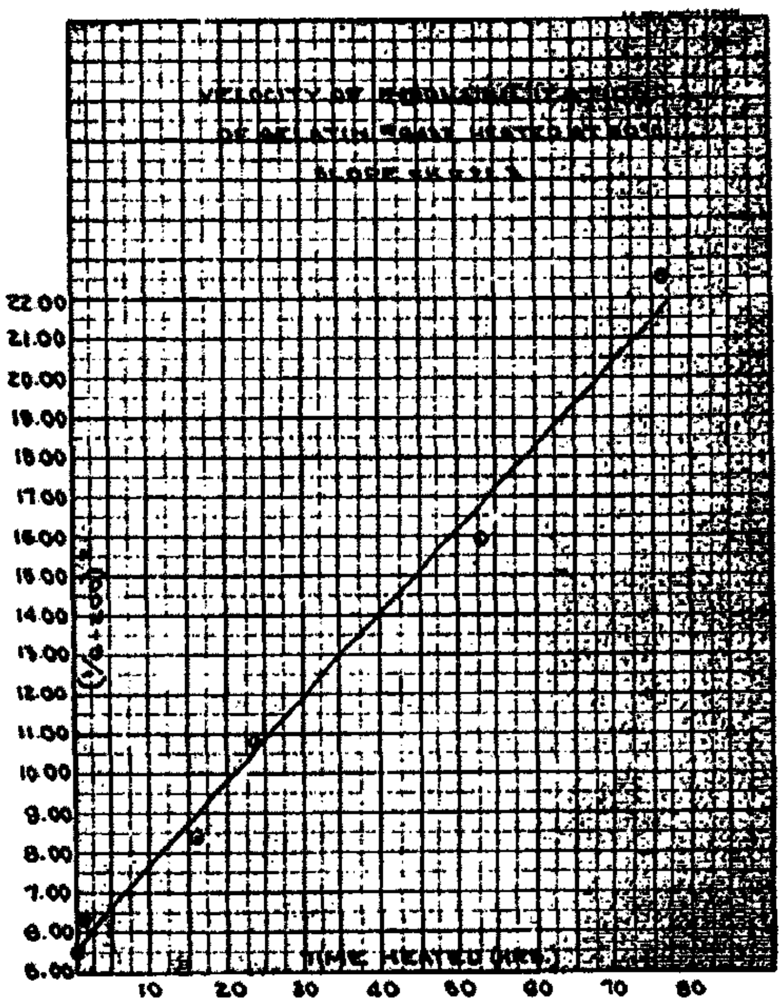
TIME HEATED (HRS.)
10
20
30
40
50
60
70
80

Fig. 2


VELOCITY OF
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21.00
20.00
19.00
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11.00
10.00
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TIME HEATED (HRS.)
10
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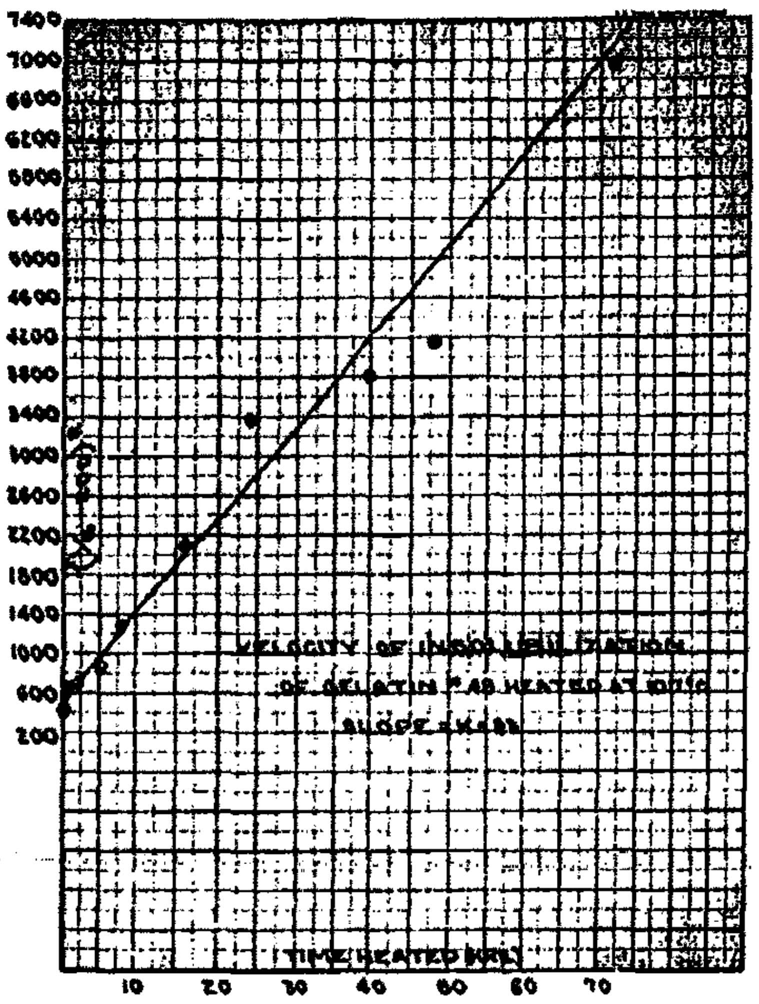
80

Fig. 3


7400
7000
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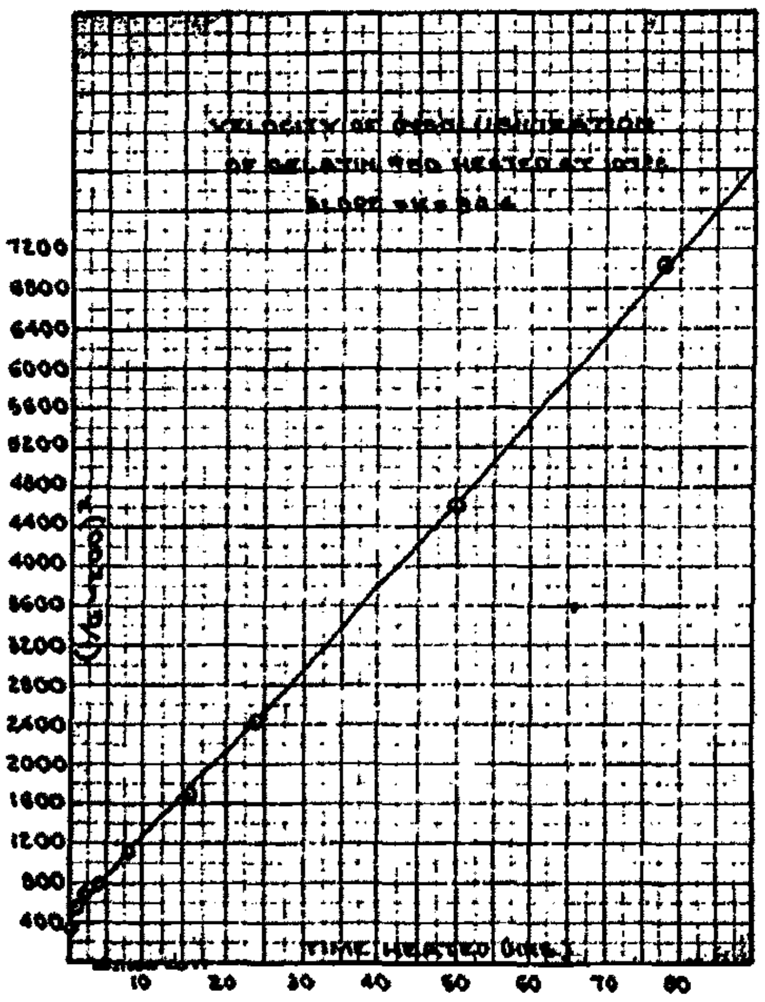
6200
5800
5400
5000
4600
4200
3800
3400
3000
2600
2200
1800
1400
1000
600
200
TIME HEATED (HRS)
10
20
30
40
50
60
70

FIG. 4


7200
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TIME HEATED (HRS.)
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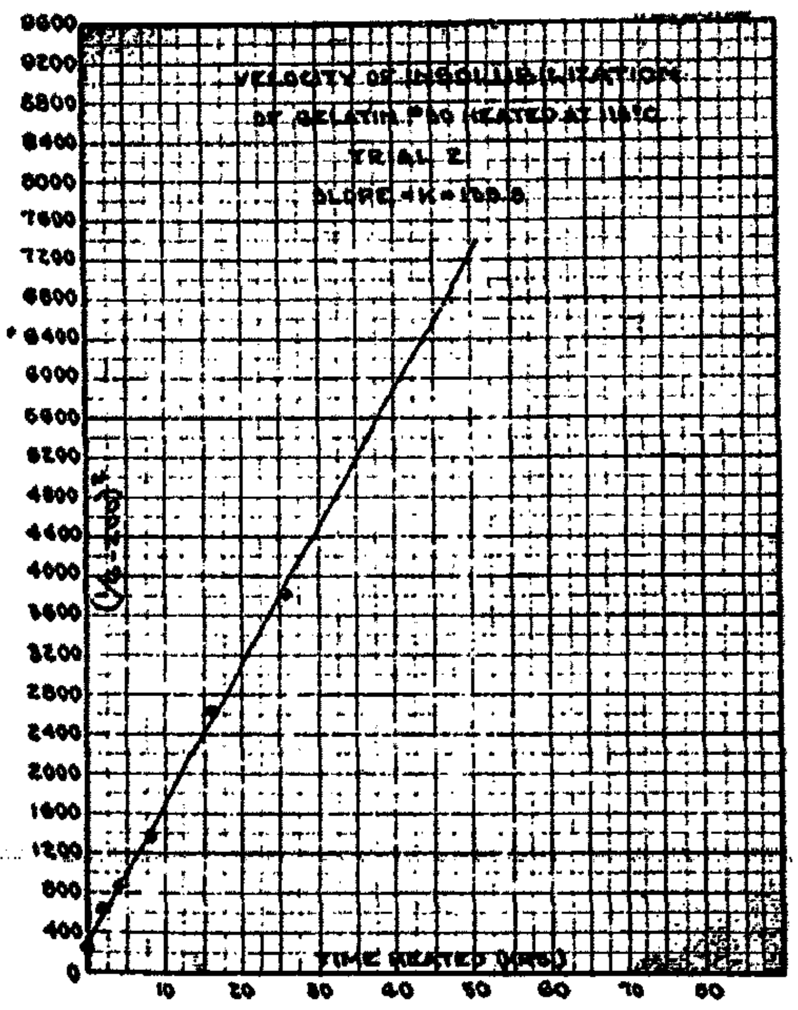
FIG. 5


VELOCITY OF INSOLUBILIZATION
TRIAL 2
9600
9200
8800
8400
8000
7600
7200
6800
6400
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5200
4800
4400
4000
3600
3200
2800
2400
2000
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400
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80
TIME HEATED (HRS)

Fig. 6

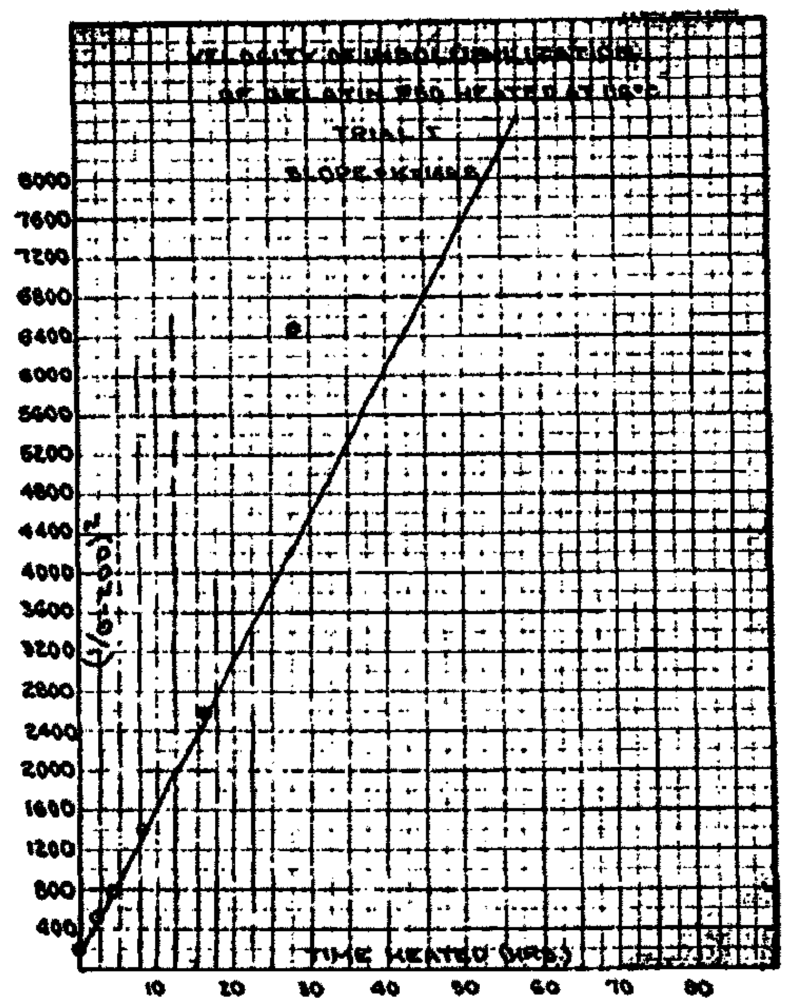
TRIAL 1
8000
7600
7200
6800
6400
6000
5600
5200
4800
4400
4000
3600
3200
2800
2400
2000
1600
1200
800
400
10
20
30
40
50
60
70
80
TIME HEATED (HRS)

Fig. 7

TABLE III

Effect of Heating at 60°C on the Swelling of Gelatin No. 50 + 4% Albumen

Time Heated in hrs.	"Equilibrium" Water Absorption
0.0	949
1.0	978
2.0	991
4.5	1000
8.0	906
16	956
24	942
48	952

TABLE IV

Velocity of Insolubilization of Gelatin No. 50 Heated at 90°C

Time Heated in hrs.	*G* % Gain in weight	G-200	1/G-200	1/(G-200)^2
0	776	576	1.73×10^{-3}	299×10^{-8}
1	733	533	1.88	353
8	699	499	2.00	400
16	616	416	2.40	576
48	520	320	3.13	979
95	430	236	4.24	1798

It appears that the expression for the termolecular reaction holds with substantial accuracy for the whole course at 90° and 107°, and for a considerable part at 116°C. The deviation here is to be expected, since after 24 hours heating at this temperature the gelatin began to yellow and give signs of charring and decomposition.

In Table V are given the velocity constants at 90°, 107° and 116°C.

TABLE V

Velocity Constants of Insolubilization of Gelatin No. 50

Temperature	Velocity Constant (Slope of 1/(G-200)^2 vs. time curve)
90°C	18.6
107°	84.4
116°	146.6 139.9 166.6 } av. 150

Applying the Arrhenius expression for the effect of temperature on the reaction

$$\frac{d \ln K}{dt} = \frac{Q}{R\,T^2}$$

in the integrated form

$$\ln \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

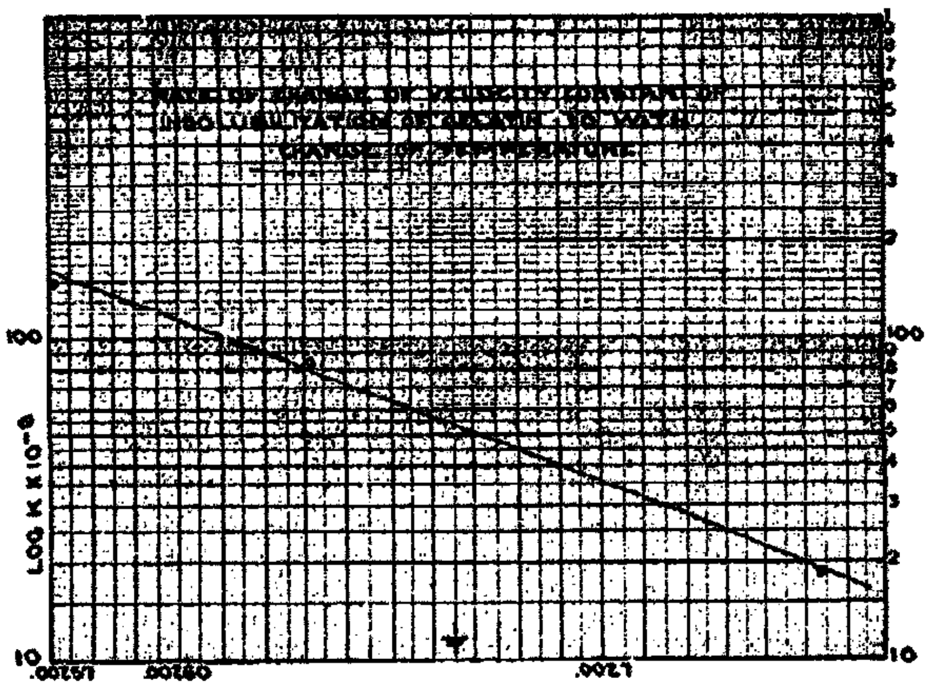

FIG. 8

then the "critical increment" Q should equal the slope of the log K vs. 1/T graph, multiplied by 2.303 × 1.98. In Fig. 8 are plotted the data from Table V. This gives Q = 23,159 calories as the "critical increment." A further justification for the end value 200 is obtained from the effect of ultraviolet light in producing insolubilization, which shows much resemblance to insolubilization by heat. Brintzinger and Maurer[8] measured the effect on degree of swelling. Using our value 200, and the termolecular expression, results shown in Table VI, and Fig. 9 were obtained, which indicate a close similarity in the reactions.

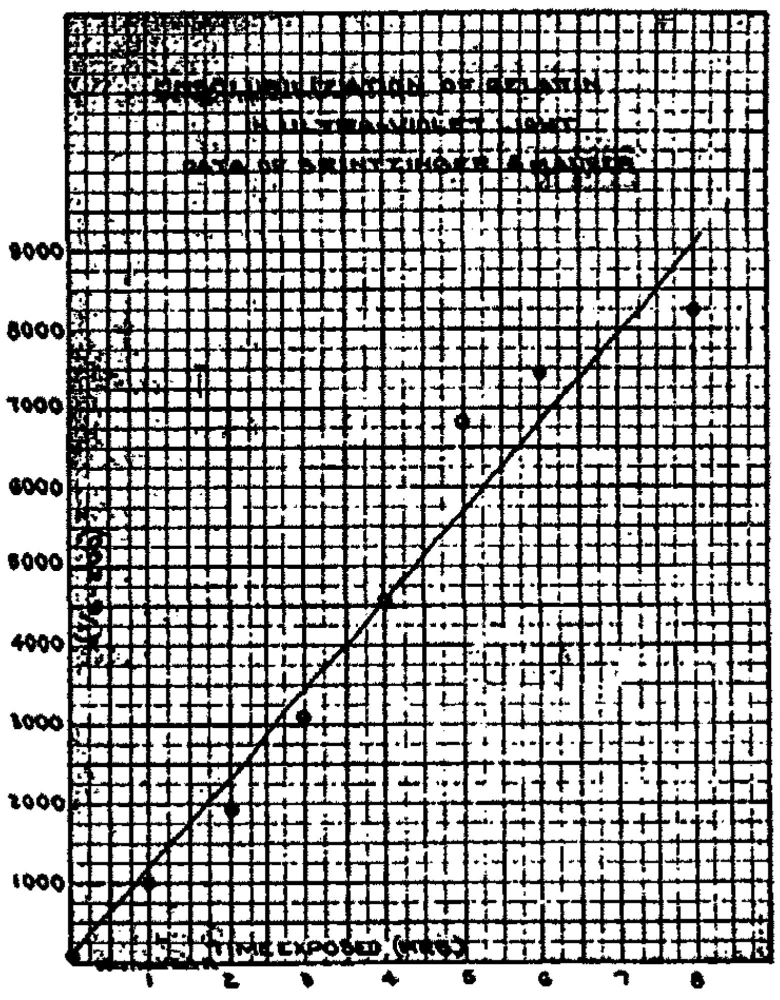

FIG. 9

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[8] Kolloid-Z., 41, 46 (1927).

TABLE VI

Velocity of Insolubilization of Gelatin by Ultraviolet Light (Brintzinger and Maurer)

Time Exposed in hrs.	G % Gain in Wt.	G-200	$\frac{1}{G\text{-}200}$	$\frac{1}{(G\text{-}200)^2}$
0	1140	940	1.06×10^{-3}	112×10^{-8}
1	512	312	3.20	1024
2	426	226	4.42	1953
3	380	180	5.56	3091
4	348	148	6.76	4569
5	321	121	8.26	6822
6	316	116	8.62	7430
8	310	110	9.09	8262

The fact that the "equivalent temperature," corresponding to the very high velocity, lies much beyond the actual temperature to which gelatin could be heated without decomposition, does not contradict this. Many photochemical reactions correspond to thermal reactions at unrealizable temperatures.

Nature of the Insolubilization Process

Desiccation of gelatin in vacuo over P_2O_5 for prolonged periods produced not more than 5% decrease in water absorption. Apparently all "free" water was removed by evacuation to constant weight (upward of 10 days) which gave the same loss of water as heating at 105°C within the error of experiment (15.1% compared to 14.9% for samples starting at same R. H.). Again, insolubilization proceeds long after apparent constant weight has been reached.

While this indicates that probably the removal of free or adsorbed water is not responsible for the insolubilization, it does not preclude a condensation, *i.e.*, elimination of H_2O between reacting groups. First, the amount of this might be small enough to fall within the error of weighing so hygroscopic a material, and second, the primary adsorption of water by dried gelatin is so powerful that it would act as acceptor for the H_2O molecules thus split off. The insolubilized gelatin does not show optically (birefringence) any marked change compared with the dried gelatin. This indicates that no specific increase in orientation has occurred, which conclusion is confirmed by lack of local intensifications in the X-ray diffraction diagram.

The interpretation of a termolecular reaction course offers some difficulties. The variable is the difference between actual water absorbing capacity at time *t* and infinite heating. The assumption that this is directly proportional to active mass of unchanged gelatin seems reasonable, but gives no clue to the termolecular course.

If gelatin jelly is dried down to adhere on a rigid support, swelling, *i.e.*, water absorption, can only take place in one direction, *viz.*, that perpendicular to the plane of the support (Sheppard and McNally)[9]. The total water absorp-

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[9] Loc. cit.

tion, however, remains practically the same. Again, if gelatin jellies are stretched some 300% and dried while so stretched, the swelling or water absorption in the direction of stretch becomes negligibly small, but the total water absorption remains the same as for unstretched gelatin. It seems possible then that for actual reduction of *total* water absorption, a reaction in *three directions* or dimensions is necessary, and that this is the significance of the termolecular order. The following discussion of cognate evidence on the fine structure of proteins, in particular of gelatin, collagen and keratin, lends perhaps some support to this hypothesis.

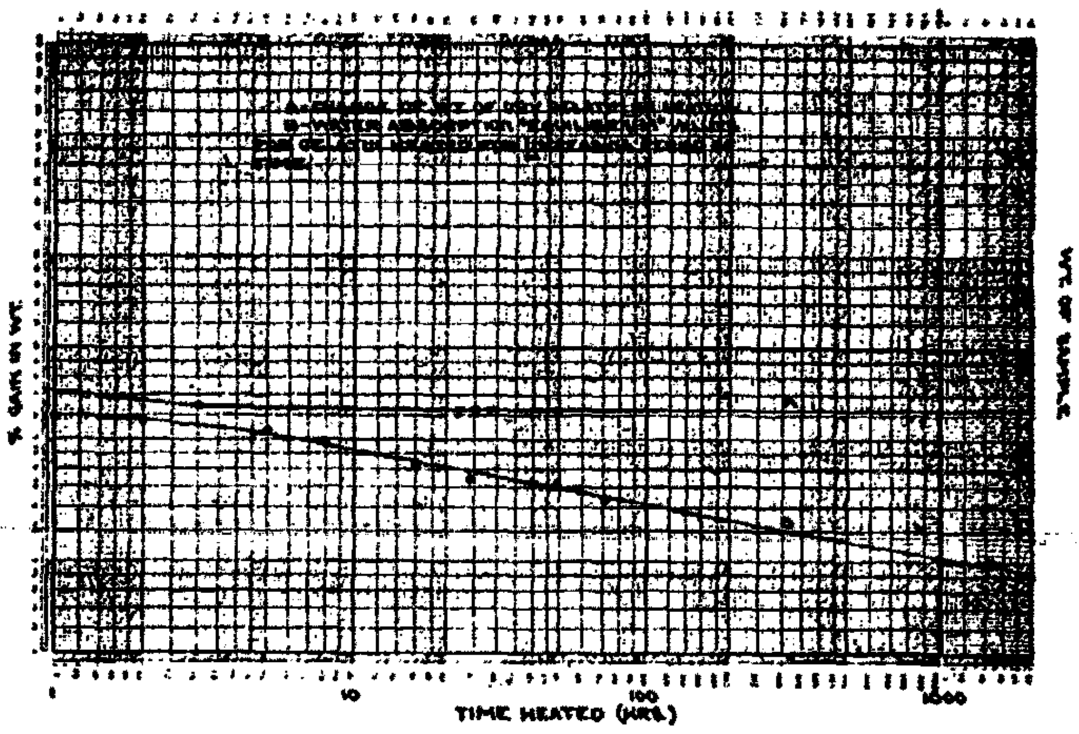

FIG. 10

Fine Structure of Proteins

We shall understand by "fine structure" the molecular and micellar constitution of the proteins as revealed or indicated by chemical investigations, by X-ray spectroscopy, and by other investigations, such as Svedberg's centrifugal separation, spreading of thin films, and the adsorption and transpiration of gases and vapors. Chemical investigation has in the main confirmed Fischer's conclusion that the proteins consist of long chain-like molecules of condensed or peptided amino-acids, a typical polypeptide chain being

$$H_2N\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot COOH.$$

This does not preclude these chains in actual proteins being branched, nor that ring formation (by anhydrization between end groups) may occur.

This conception has been confirmed and made much more specific by recent X-ray investigations.[10] Briefly, these indicate that the natural proteins consist of more or less uniformly oriented crystallites (primary micelles) of parallel polypeptide type chains. In the case of silk fibroin the chain may be represented as

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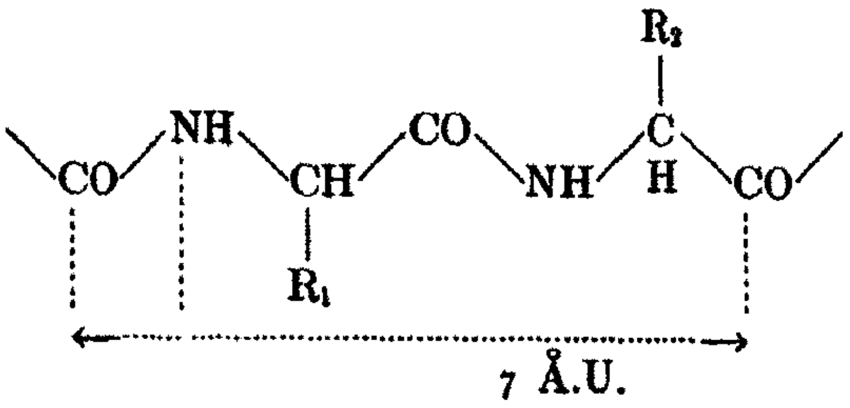
[10] *Cf.* Meyer and Mark: "Der Aufbau der hochpolymeren organischen Naturstoffe" (1930); Astbury and Woods: J. Textile Inst., 23, T17 (1932).



It is the $-C-NH-CH-$ repeating unit which gives dimensional regularity and similarity, the side chains R_1, etc., which in the first place provide differentiation. The following proteins have been found to give diagrams interpretable in this general sense:— silk fibroin,[11] keratin in wool and hair,[12] collagen in sinews,[13] and to some extent in hide,[14] gelatin.[15] It is to be noted that all these belong to the so called sclero-proteins, not dispersing in water or aqueous solutions, with the exception of the derived protein, gelatin. Of these, silk fibroin is composed principally of glycine and alanine. Primary valence (polypeptide) chains of these in alternating order are arranged in parallel bundles as crystallites or micelles. There is also an amorphous, or non-oriented material which can be extracted with formic acid. For the crystalline part observations permit of the calculation of a monoclinic cell[16] characterized as

$$a = 9.68 \text{ Å.U.}$$
$$b = 7.00 \text{ Å.U.}$$
$$c = 8.80 \text{ Å.U.}$$
$$\beta = 75^\circ 50'$$

The interval b = 7.00 Å.U. is the identity period along the fiber axis. The assumption of 4 alanyl-glycyl chains for the elementary cell leads to a density of 1.46, as compared with 1.33 to 1.46 observed. The distances of the principal chains from each other, $1/2\ a = 4.8$ Å.U. and $1/2\ c = 4.4$ are as usually found.

Meyer and Marks[17] remark that "Der hohe Zusammenhalt der Peptidketten und der Mizelle aneinander erklärt sich durch die besonders hohe Molkohäsion der CONH-Gruppe (10,600 cals)." Assuming that the molar cohesion of a glycyl residue is about 11,000 cals, a chain of 100 peptide residues of length of 350 Å.U. would have a molar cohesion of over 10^6 cals, which approaches that of a cellulose chain. The similarity of silk and cellulose fibers in respect of tensile properties rests on analogous constitution and micellar (lattice) forces.

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[11] Kratky: Z. physik. Chem., 5, 297 (1929).

[12] Astbury et al: Loc. cit.; Abitz: Dissertation, Leipzig (1930).

[13] Herzog and Jancke: Ber., 53, 2162 (1920).

[14] Gerngross and Katz: Loc. cit.

[15] Ibid.

[16] Cf. Meyer and Mark: Op. cit. p. 222.

[17] Op. cit., p. 223.

While cellulose and silk fibroin show no special features under mechanical or thermal treatment, rubber, keratin (of wool and hair), and collagen (sinew) exhibit notable pecularities. Thus, rubber only shows a well defined fiber pattern on considerable stretching. On the other hand,[18] keratin of wool and hair shows one pattern, with an identity period in the fiber direction of 5.1 Å.U. for unstretched material (α-keratin), and another for stretched material. The α-keratin chain of 5.15 Å.U. period appears to change into a chain with two definite halves when stretched to 6.64 Å.U., *i.e.*, to show two halves of 3.32 Å.U. This extension of 29% corresponds to actual 30% extension. Its limits of elastic extension is 100%, close to 3 × 3.32 Å.U. This intramolecular displacement is diagrammatically typified in Fig. 11.

β-keratin, silk fibroin, and in some degree collagen, and stretched rubber have fully extended chains, while unstretched hair (α-keratin) and unstretched rubber, and, perhaps, *heated* collagen (sinew) have "folded" chains.

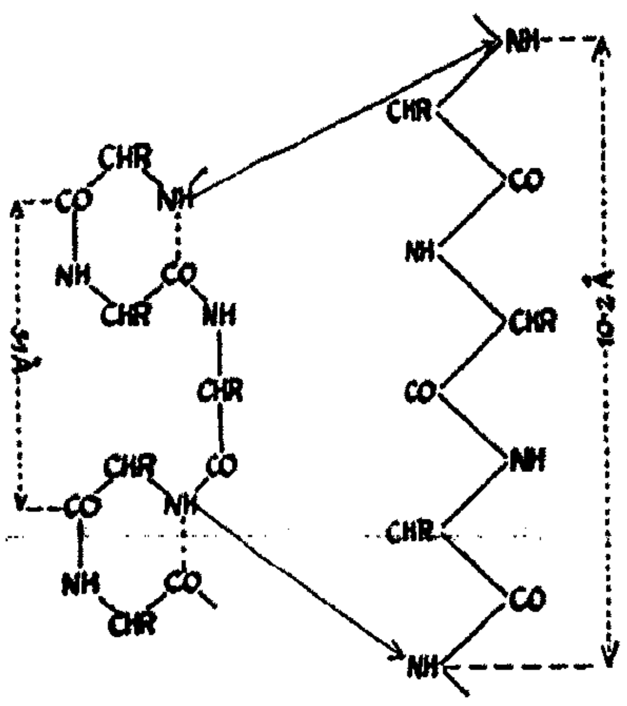

FIG. 11

Intermolecular and Intramolecular Forces

The great strength of fibers is to be attributed to the intermolecular forces, or molar cohesion of the chains.[19] It appears, however, that this, at any rate with the "extended" type of chains, is not enough to prevent intramicellar swelling by water, and, by reason of the consequent loss of molar cohesion, peptization and solution at sufficient temperature to destroy orientation. This is what occurs with gelatin, not only ordinarily dried gelatin, but gelatin *stretched 200 to 300%*, which gives a partly "fibrous" diagram practically identical with that from collagen. Yet collagen itself, though taking up 200% of water, does not peptize or dissolve in water at temperatures such as gelatin does, but requires nearly boiling water. There are a number of phenomena with these materials which make it a probable, if not a necessary assumption, that a certain degree of intramolecular binding occurs between chains. Speakman and Hirst[20] explaining the action of acids in lowering the work required to stretch wool fibers (compared to water at the isoelectric point) suggest linkages of the *free* amino groups of the diamino-acids-arginine and leucine—with the *free* carboxyl groups of dicarboxylic acids—aspartic and glutamins. This would give a bridge of the type

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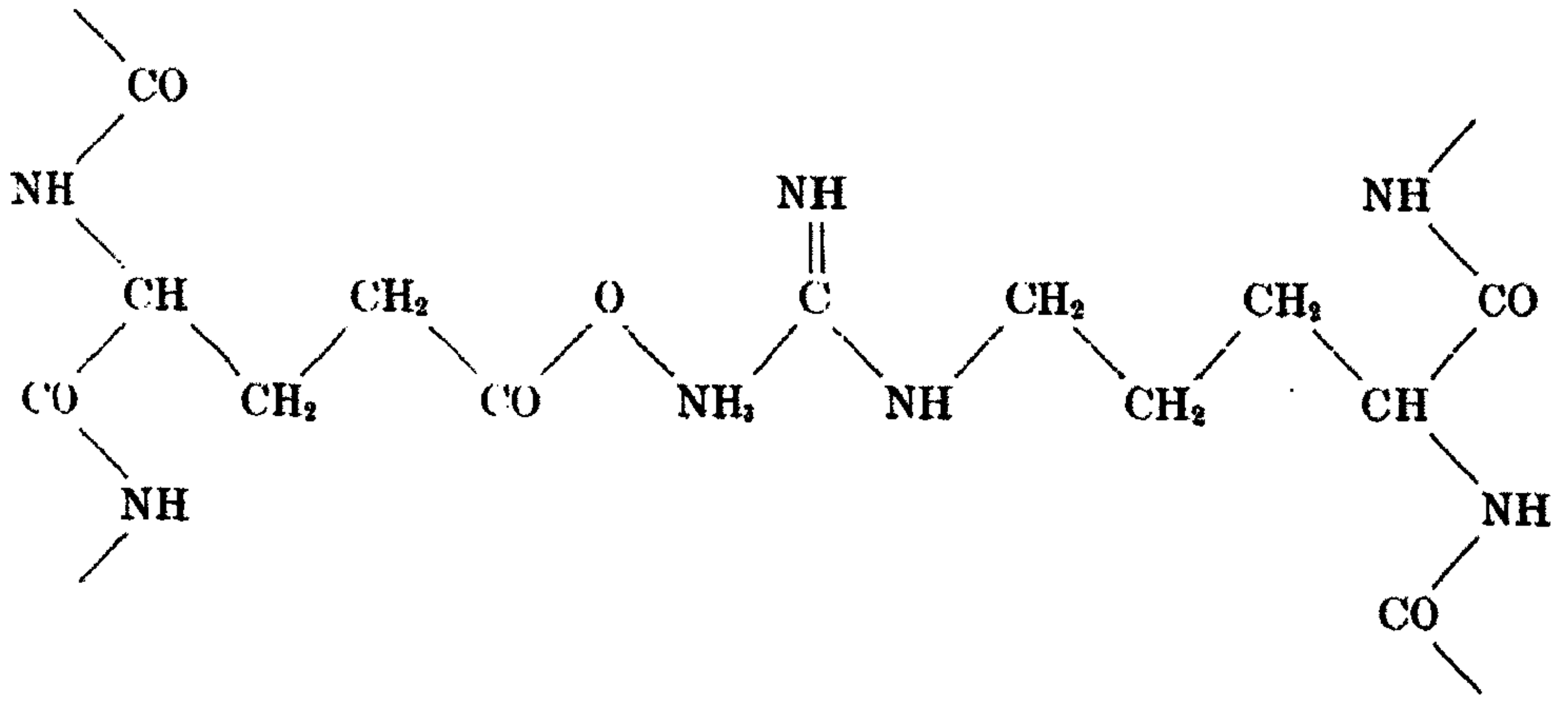
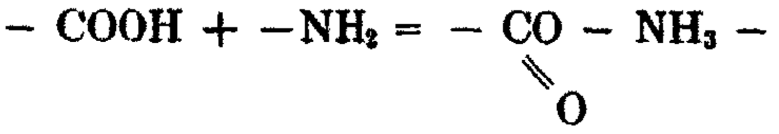
[18] Astbury and Woods: Loc. cit.

[19] Meyer and Mark: Loc. cit., p. 223.

[20] Nature, **128**, 1074 (1931).



Evidence for an intermolecular period of -27 Å.U.—about twice that given by the above, has been found by Astbury in wool, while Speakman shows that the heat of formation of the linkage



$$-\mathrm{COOH} + -\mathrm{NH_2} = -\underset{\setminus\!\!\setminus \mathrm{O}}{\mathrm{CO}} - \mathrm{NH_3} -$$

would be of the order of the work difference of stretching in acid and water -1.2 kg calories. Astbury and Woods[21] have also suggested cross linkages of sulfur atoms (from cystine) and of anhydrides of the free carboxyls of dicarboxylic acids.

So far, these interlinkages have been proposed as occurring between the parallel chains of the crystallites proper. This should be capable of verification by X-ray spectroscopy in conjunction with swelling experiments. Attention may be drawn to the possibility of condensations and interlinkages occurring between the fringe-like ragged or unoriented extensions of the crystallites, evidence for the existence of which exists to some extent in the so-called amorphous, non-crystalline portions of fibrous materials.[22]

It appears to us that such interchain or intermolecular linkages may be assumed to account for the difference between collagen and gelatin. The relatively high critical increment indicated by the temperature velocity coefficient points to more than a neutralization of $-\mathrm{NH_2}$ by $-\mathrm{COOH}$ groups. It is true that this heat value—25,000 cals.—probably does not refer to a specific heat formation of a substance or linkage. If the reaction is a condensation, the "critical increment" from kinetic considerations will be the sum, or difference, of heats of activation and true heat of reaction (heat of formation of products). If the insolubilization of gelation by ultraviolet—necessarily of wave-length shorter than 3600 Å.U.—may be regarded as involving a quantum of that order for activation, this would mean about 70,000–90,000 cals., which is of the same order as the predissociation energies of certain organic molecules.

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[21] Loc. cit.

[22] Cf. Abitz: Roentgenographische Struckturforschung des Gelatine-micells. Dissertation, Leipzig (1930).

On this view the actual reaction concerned in the insolubilization of gelatin would be generating heat, but considerably less than the activation heat required.

The Effect of Additions on the Insolubilization of Gelatin

It has been suggested by Northrop and Kunitz[23] that the swelling phenomena of gelatin in water at the isoelectric point can be interpreted in terms of the osmotic pressure of a soluble gelatin encased in capsules of an "insoluble" gelatin. Evidence has been produced by Sheppard and Hudson[24] that the insoluble gelatin fraction separated by Kunitz and others is an albuminous impurity, occurring in amounts varying from 0.2 to 1.5% in commercial gelatin. It has a different chemical composition, and is coagulated by heat in weakly acid solution (pH 4.7). The present authors expect to publish data showing other difficulties for this theory of swelling. The possibility, however, that the observed insolubilization of gelatin might depend upon a coagulation of this dispersed albumin in gelatin led us to test the effect of addition of

(a) egg albumin
(b) gelatin albumin

upon the heat insolubilization. The results did not support the view that the insolubilization of gelatin is in any way caused by coagulation of a foreign protein.

Insolubilization and Denaturation

In some respects the insolubilization of gelatin might be assimulated to the coagulation and denaturing of albumins. Miss Galinsky[25] in an interesting paper on "The Effect of Light and Salts on Gelatin" states that exposure of a dichromated gelatin solution to light, followed by precipitation in acetone, gives an insoluble gelatin which is ash-free, *i.e.*, contains no chromium. This gelatin was chemically indistinguishable from the soluble original, and its production is regarded as similar to the coagulation of albumin. We hope to compare this insoluble gelatin with that produced by direct action of heat and of light. Provisionally it appears probable that the dichromate first acts as a photochemical (optical) sensitizer for the insolubilization, and is subsequently reduced.

Gelatin insolubilized by heat may be reverted, *i.e.*, converted to soluble gelatin, by treatment with boiling water. The regenerated gelatin had similar but slightly higher swelling values than the original. We shall show elsewhere that this is probably caused by a greater proportion of hydrolyzed gelatin.

Summary

Gelatin on prolonged heating at sufficiently elevated temperatures progressively loses swelling power and its solubility in warm water. A quantitative study has been made on this behavior; the results extend the conception of collagen and gelatin as high molecular compounds and clarify their rela-

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[23] Kunitz and Northrop: J. Gen. Physiol., **12**, 384 (1928).

[24] Sheppard, Hudson and Houck: J. Am. Chem. Soc., **53**, 760 (1931).

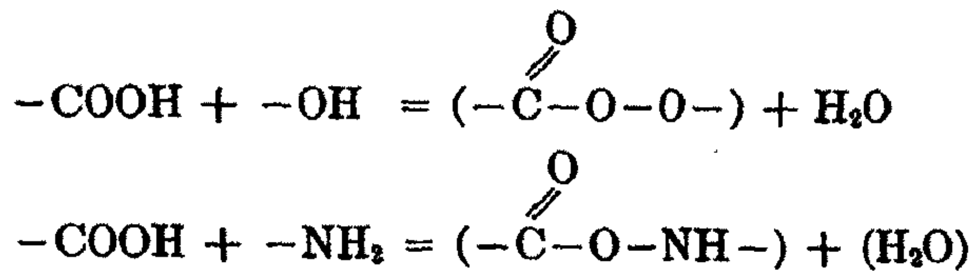
[25] Biochem. J., **24**, 1706 (1931).

tionship. The rate of insolubilization, as measured by reduction of swelling capacity (water absorption) is a marked function of temperature. The reaction follows a termolecular order; from the temperature coefficient, in the Arrhenius expression $\frac{d \ln K}{dt} = \frac{Q}{R\,T^2}$, Q the critical increment of insolubilization was found to be 23,160 calories.

Insolubilization by ultraviolet light was found to follow the same reaction course, though at greater velocity than that at the highest temperature studied (116° C).

The insolubilized gelatin resembles collagen (a) in having the same water absorption, and (b) in being converted to gelatin by extraction with hot water. It differs in not showing the X-ray diagram of collagen, nor optical birefringence. If gelatin jellies (made with much alcohol) are stretched several hundred percent, and dried at room temperature, the dried material is optically anisotropic and gives the X-ray diagram of collagen. Although it swells very little in the direction of stretch, its total water absorption is the same as for unstretched gelatin. By heating this stretched gelatin to insolubilization, a material is produced having substantially all the physical characteristics of collagen.

It appears probable, therefore, that the conversion of collagen to gelatin involves something more than the disorientation of long chain molecules assembled in crystallites. The facts suggest hydrolytic disruption of definite chemical interlinkages between these long chains. These linkages, causing some degree of two-dimensional and three-dimensional polymerization or macromolecule formation, confer insolubility and greatly restricted intramicellar water absorption. A reaction of the types



$$-COOH + -OH = (-\overset{\overset{O}{\|}}{C}-O-O-) + H_2O$$

$$-COOH + -NH_2 = (-\overset{\overset{O}{\|}}{C}-O-NH-) + (H_2O)$$

between side groups of the primary molecular chains would account for the phenomena; they would thereby be brought into line with the vulcanization of rubber, the "permanent set" of steamed hair, and perhaps other changes in high molecular substances.

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COLLOID CHEMISTRY OF ASPHALTS

BY CHARLES MACK

Zsigmondy made the following statement—"we are accustomed in chemistry to ask investigators who speak of the existence of a chemical compound to give proofs of its existence, its make-up, and its detailed description." In the application of this statement to asphalts, we find that our knowledge of this material is very poor and empirical.

If we consider asphalt as belonging to the realm of colloid-chemistry, it must be studied from both the chemical and physical aspect, since the colloidal state is an intermediate one between physics and chemistry.

Chemistry of Asphalts

According to Marcusson[1] asphalt is composed of five groups of compounds: Oily constituents; asphaltic resins; asphaltenes; carbenes and carboids; asphaltic acids and anhydrides.

Oily Constituents. The oily constituents may be separated from asphalt by first mixing the latter with Fuller's earth or some adsorption clay and then extracting the mixture with petroleum ether. These compounds appear as a viscous oil similar to cylinder oil and are usually fluorescent. They are hydrocarbons, and generally contain small percentages of sulphur and oxygen.

Asphaltic Resins. The asphaltic resins represent the intermediate products formed in the transformation of oily constituents into asphaltenes by oxidation with air. They are solid with a softening point of 100° C or higher. They vary from reddish to dark brown in colour. When adsorbed by clay they cannot be extracted with petroleum ether. The adsorption clays polymerize the asphaltic resins with partial formation of asphaltenes. The best method for their separation is due to Sachanen.[2] The asphaltic acids are first of all extracted from a solution of asphalt in 5 parts of benzene by means of alcoholic potash solution. After having washed out the benzene layer with water the asphaltenes are precipitated with petroleum ether. The remaining solution which contains the resins and oily constituents is treated with silica gel in the ratio of 100 parts of silica gel to 1 part of resins. The oily constituents are extracted with light naphtha and the adsorbed resins with chloroform.

Sachanen found that the molecular weights of the resins depend upon the molecular weights of the oils from which they are derived, and that they are always somewhat higher than the molecular weights of the oily constituents. The resins contain oxygen and are oxidation products of the oily constituents and not products of condensation. Resins form true solutions with certain solvents.

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[1] "Die natuerlichen und kuenstlichen Asphalte" (1931).

[2] Sachanen and Wassiliew: Petroleum Zeit., 23, No. 36, 1618 (1927).

Asphaltenes. Asphaltenes are formed from asphaltic resins by further action of sulphur or oxygen. They appear as a dark brown to black powder. On heating they do not melt but swell. Their specific gravity is higher than 1. They are soluble in benzene, chloroform, carbon tetrachloride and insoluble in ether, petroleum ether and alcohol. Before they dissolve in the solvents mentioned above they swell. By evaporation of these solutions homogeneous solutions of high concentrations can be obtained which set to gels at lower temperatures. In contrast to the asphaltic resins the asphaltenes form colloidal solutions.

Chemically speaking, the following reactions are characteristic for asphaltenes as well as for asphaltic resins: When treated with fuming nitric acid they are changed into nitro-compounds soluble in acetone, which after treatment with alcoholic potash solution become soluble in water. The alkali salts of these nitro-compounds are precipitated by calcium chloride, silver nitrate, etc.

Asphaltic resins and asphaltenes form addition products with sulfuric acid. They are oxidized by potassium permanganate to acids. They do not react with diazo-compounds nor with phosphorus pentachloride, but form molecular compounds with mercuric bromide and ferric chloride. They cannot be saponified and show only small acetyl numbers. According to these properties asphaltenes and asphaltic resins do not appear to react like acids, esters or lactones, or to contain alcoholic or phenolic hydroxy or oxy-groups.

Poell[3] has shown that the determination of iodine numbers on asphalts and lubricating oils have no meaning since the amount of iodine taken up can be found as hydriodic acid. This would indicate that no double bonds are present, and that in these cases iodine substitutes hydrogen. The chemical properties of the asphaltenes and asphaltic resins seem to indicate that they are polycyclic compounds containing oxygen and/or sulfur in bridge or heterocyclic linkage. Generally speaking, however, it is difficult to definitely establish the structure of compounds of high molecular weight from their chemical reactions.

Carbenes and Carboids. These compounds are present in petroleum asphalts only in minute quantities. Whereas, the carbenes are soluble only in carbon bisulphide, the carboids are totally insoluble in all solvents. They are obtained when asphalt is dissolved in cold carbon tetrachloride. The material insoluble in this solvent represents a mixture of carbenes and carboids. The solubility of the carbenes in carbon bisulfide is used as a means of separating them from the carboids.

In their chemical reactions with sulfuric acid, nitric acid, ferric chloride, mercuric bromide, etc. the carbenes and carboids behave like asphaltenes, and appear to be condensation or polymerization products of asphaltenes.

Asphaltic Acids and Their Anhydrides. They are present in petroleum asphalts in small percentages only, in contrast to natural asphalts, which contain them in larger percentages, as high as 12%. The asphaltic acids are separated from asphalts by cold extraction of a solution of asphalt in benzene

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[3] Petroleum Zeit., 27, No. 45, 817-826 (1931).

with alcoholic potash solution. Having removed the asphaltic acids their anhydrides can be extracted as acids from the asphalt solution in benzene after saponification.

The asphaltic acids are brownish black in colour and form a tar-like or resinous mass usually containing sulphur. When heated to 120°C they are converted into the corresponding anhydrides and at higher temperatures are transformed into unsaponifiable substances.

Colloid Chemistry of Asphalts

The three main constituents of asphalts are asphaltenes, asphaltic resins and oily constituents. Asphalt forms a lyophilic sol. In our investigations we have considered the asphaltenes as the dispersed phase and the mixture of asphaltic resins and oily constituents as the dispersion medium. For simplicity this mixture of asphaltic resins and oily constituents will be referred to as "petrolenes," the term which is generally used.

Lyophilic Sols are characterized by: (1) Their relative stability; (2) difficulty in detecting particles of the disperse phase under the ultramicroscope; (3) high viscosity, often exhibiting elastic properties; (4) the property of forming gels; (5) low solubility of the solute in the solvent at the temperature of gel formation.

With respect to the first characteristic, asphalts generally represent a stable system. Investigations by Holde[4] have shown that asphaltenes in solution are amicroscopic under the ultra-microscope.

Viscosity of Asphalts

One of the most important properties of asphalts is viscosity, since in practice the specifications for asphalts are generally expressed in terms of viscosity such as softening point and penetration. The softening point is defined as the temperature at which an asphalt that has been poured into a brass ring of standard size becomes soft enough to allow a steel ball of standard size to fall through it. The penetration of an asphalt is the distance measured in tenths of millimeters which a needle loaded with 100 grams will penetrate during 5 seconds under standard temperature conditions.

Penetrations are generally taken between 0 and 37.8°C. The viscosities of the asphalts studied were determined over the same temperature range since their viscosities at these temperatures are of importance with respect to their behaviour on the road.

For the determination of viscosity at low temperature, Pocchetino's falling cylinder apparatus[5] has been used. The apparatus consists of two vertical coaxial cylinders, the clearance between the cylinders being 0.0075 cm. The asphalt is poured between the cylinders to a certain height. The inner cylin-

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[4] Z. angew. Chem., 21, 2143 (1908).

[5] Nuovo Cimento, 8, 77.

der is loaded with weights and the velocity with which it descends is measured. The viscosity is calculated from the following integrated formula:

$$N = \frac{P}{2\,\pi L v} \ln \frac{R_2}{R_1} \qquad (1)$$

where N = viscosity in poises; P = total weight; v = velocity; L = length of tube of asphalt; R_2 = radius of outer cylinder; R_1 = radius of inner cylinder.

To study the influence of the concentration of asphaltenes upon the viscosities of asphalt, the asphaltenes were separated from the mixture of asphaltic resins and oily constituents (petrolenes) in the following way:

The asphalt was shaken with 50 parts of petroleum ether until the petrolenes were dissolved and the solution was then allowed to stand for 48 hours in the dark. The extract was filtered from the asphaltenes. The asphaltenes were washed with petroleum ether until the filtrate was colourless. To free the asphaltenes from the last traces of resins they were dissolved in 10 parts of benzene and precipitated with 100 parts of petroleum ether. The procedure was then repeated. The different extracts of the asphaltenes were combined and filtered through an ultra-filter in an atmosphere of carbon dioxide. The ultra-filter was prepared from a hard filter paper by first treating it with a 2% solution of collodion in an ether-alcohol mixture and while still wet, coagulating the collodion with petroleum ether. The filtrate was then freed from the solvent by distillation removing the last traces under vacuum at 200°C. The petrolenes thus prepared were found to be free from asphaltenes.

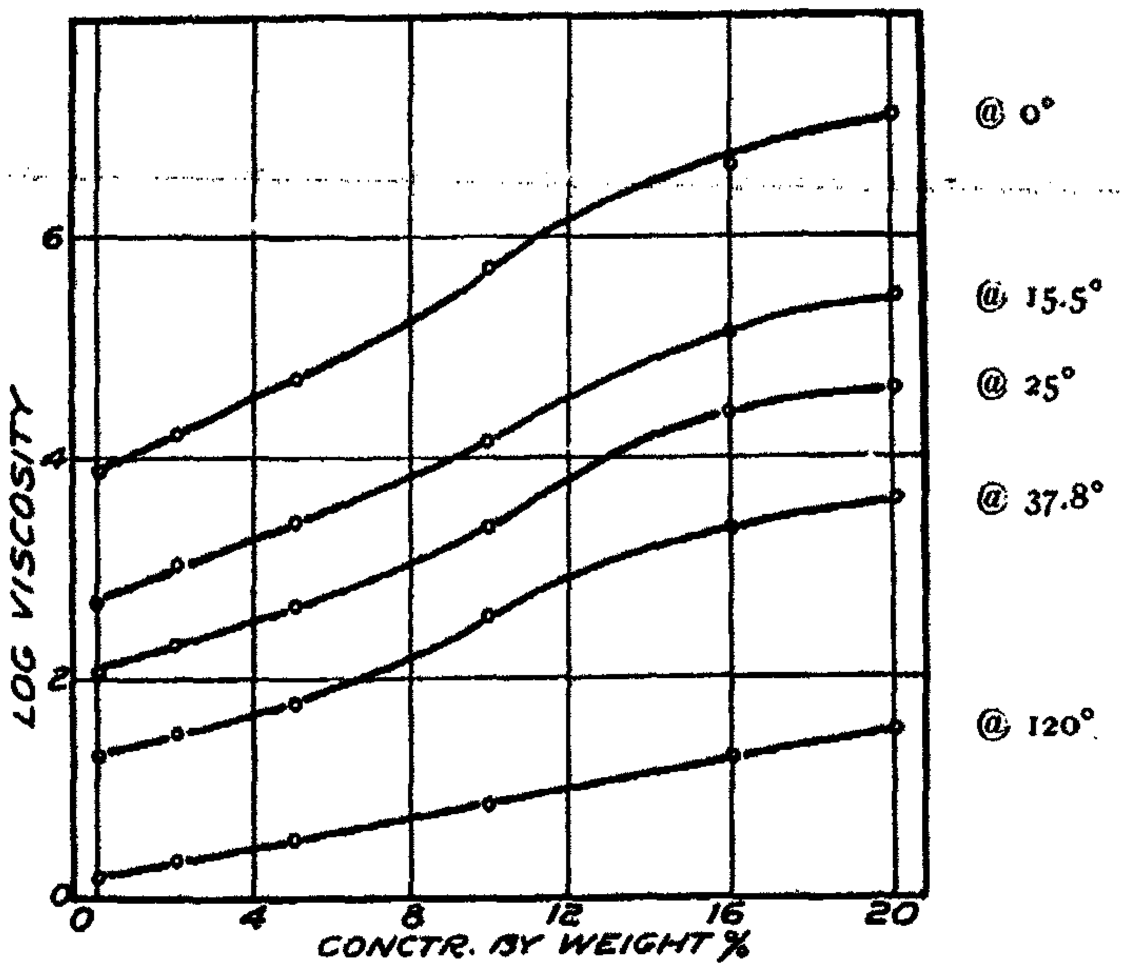

FIG. 1

Solutions of Asphaltenes in Petrolenes log. visc. vs. concentration. Visc. at 120°C in poises, visc. between 0 and 37.8°C in gr. sec. cm^{-2}.

In Table I, the viscosities are shown for mixtures of asphaltenes and petrolenes obtained from a blown Mexican asphalt of a softening point of 64°C. Asphaltenes separated by the usual method from asphalt must be kept in solution in benzene because if they are dried after precipitation with naphtha they cannot be re-dissolved in the petrolenes.

Structural viscosity has not been found to occur in these mixtures. By loading the inner cylinder of the falling cylinder apparatus with different weights, thus varying the velocity gradient, the same viscosity coefficients were obtained, within the allowable experimental error. The discontinuity of the log viscosity-concentration curves (Fig. 1) would indicate that structural viscosity occurs at concentrations between 10 and 20%. However, a sphere of about 1 cm diameter of the mixture containing 20% of asphaltenes spreads in about 5 hours on a plate at room temperature, indicating that this mixture is a liquid of high viscosity and not a plastic material.

From Table II it will be readily seen that relative viscosity increases with falling temperature and increased percentage of asphaltenes, *i.e.*, at 0°C from 2.13 for a 2% sol to 1792 for a 20% sol.

From this fact, and taking into consideration the formation of colloidal solutions of asphaltenes in benzene, it may be concluded that the asphaltenes are present in asphalts in colloidal state in the form of the emulsoid type. The concept of asphalts being stable suspensoid sols must necessarily be rejected, since the temperature coefficient of relative viscosity in lyophobic sols is merely that of the dispersion medium.

TABLE I

Viscosity of Sols of Asphaltenes in Petrolenes in Poises

% Asphaltenes	@ 0°C	@ 15.5°C	@ 25°C	@ 37.8°C	@ 120°C
0%	7.44×10^6	4.70×10^5	1.10×10^5	1.86×10^4	1.645
2%	1.59×10^7	1.03×10^6	2.00×10^5	2.89×10^4	2.226
5%	5.03×10^7	2.48×10^6	4.65×10^5	5.59×10^4	3.437
10%	5.35×10^8	1.35×10^7	2.20×10^6	3.61×10^5	7.094
16%	4.44×10^9	1.38×10^8	2.22×10^7	2.17×10^6	18.85
20%	1.33×10^{10}	2.79×10^8	4.03×10^7	4.18×10^6	33.11

TABLE II

Relative Viscosities of Asphaltenes in Petrolenes

% Asphaltenes	0°	15.5°	25°	37.8°	120°
2	2.137	2.136	1.82	1.552	1.353
5	6.76	5.281	4.23	3.00	2.09
10	71.82	28.81	20.01	19.37	4.312
16	596.4	294.1	201.8	116.2	11.45
20	1792.3	592.9	367.0	224.2	20.12

The Concentration Function

Since relative viscosity is a function of particle size, an attempt was made to apply several of the formulae dealing with the relationship between relative viscosity and concentration.

By a re-arrangement of Einstein's formula

$$N_s = N\,(1 + 2.5\ c) \qquad (2)$$

where N_s = viscosity of suspension; N = viscosity of dispersion medium; c = concentration of dispersed phase expressed as volume of suspensoid in unit volume of suspension, we obtain

$$N_s/N - 1 = 2.5\ c \qquad (3)$$

The expression on the left hand side of the equation represents "relative viscosity − 1" and is the viscosity by which the viscosity of the dispersion medium is increased under the influence of the dispersed phase. Staudinger[6] calls this expression "specific viscosity" and denotes it by means of the following formula:

$$N\ \mathrm{spec} = c\ \mathrm{Km}\ M \qquad (4)$$

where N spec = specific viscosity; c = concentration; M − molecular weight of the solute; and Km = a constant which has to be determined from viscosity data of the lower members of homologous rows.

The application of this formula to the viscosity data of asphalt may be best illustrated by means of an example. The values of N spec/c for a 2% solution of asphaltenes in petrolenes are 0.176 at 120°C and 1.068 at 0°C. Since Km is a constant the molecular weight of the asphaltenes must be 1.068/0.176 = six times higher at 0°C than at 120°C. It is evident that this is impossible with relative viscosities of 2.137 at 0°C and 1.353 at 120°C.

Arrhenius' formula[7]

$$N/N_0 = K^c \qquad (5)$$

in which N_0 = viscosity of solvent; N = viscosity of solution; c = concentration; K = a constant, does not take into consideration the molecular weight of the solute, and has not always been found to agree with the facts.

Kendall and Monroe[8] have chosen compounds which form ideal solutions to ascertain the relation between viscosity and concentration. They have carried out viscosity measurements on naphthalene solutions in benzene and toluene at 25°C. The freezing points of these solutions have been determined by these investigators and found to be in agreement with the law of ideal solutions. Kendall and Monroe derived from their measurements a formula showing the viscosities of the solvent and of the solute to be additive which was found to give good results for the viscosity concentration relationship. However, since the viscosity of the solute differs with different solvents, this relationship has no meaning at all.

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[6] Ber., **63**, 222 (1930).

[7] Medd. Vetenskapsakad. Nobelinst., **3**, No. 21 (1917).

[8] J. Am. Chem. Soc., **39**, 1802 (1917).

It was therefore very desirable to develop a formula connecting viscosity with concentration from which the molecular weight of the solute could be calculated. As far as it is known, a valid formula of this kind has not yet been published.

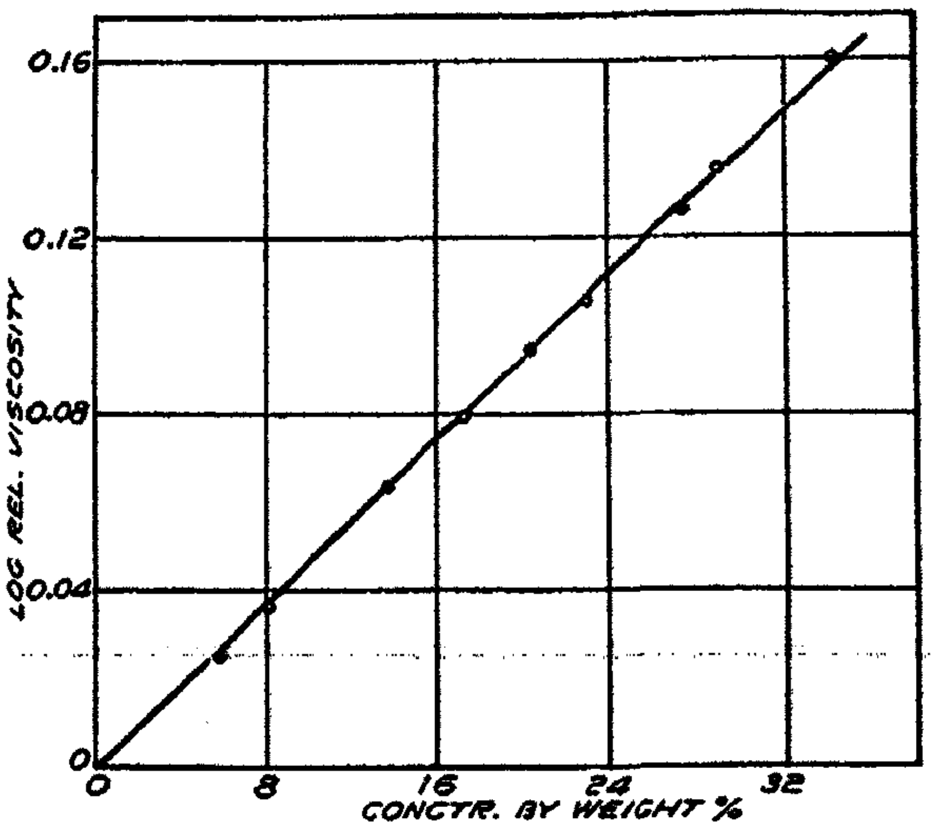

Fig. 2

Log. relative viscosity vs. conctr. in percent by weight.
○ Naphthalene in Benzene
● Naphthalene in Toluene

Table III

Viscosities of Solutions of Naphthalene in Benzene and Toluene in Centipoises (Temp. 25°)

(Kendall and Monroe)

Naphthalene in Benzene		Naphthalene in Toluene	
% of solute in solution	Absolute viscosity in c.p.	% of solute in solution	Absolute viscosity in c.p.
0.0	0.6048	0.0	0.5526
8.11	0.6565	5.73	0.5848
17.16	0.7261	13.72	0.6394
22.97	0.7707	20.12	0.6866
28.82	0.8263	27.31	0.7470
34.10	0.8764		

For these investigations Kendall and Monroe's data on naphthalene solutions has been chosen (Table III).

It has been found that when the logarithms of the relative viscosities for the solutions of naphthalene in benzene are plotted against concentration, a straight line is obtained upon which the logarithms of the relative viscosities for naphthalene in toluene are found to fall (Fig. 2). Since the straight line goes through the zero point the mathematical expression for the viscosity concentration curve is $y = e^{ax}$, and the formula for the viscosity concentration relationship reads

$$\log \text{rel. viscosity} = c\,K \qquad (6)$$

where "c" is the concentration in weight percent and "K" a constant.

The same formula is also obtained in another way. The logarithms of the absolute viscosities for these solutions plotted against concentration form a straight line. The absolute viscosities of solutions as a function of the concentration can be represented by $y = ae^{kx}$. Since "a" is a function of "y" when $x = 0$, the exponential equation reads $y = y_0e^{kx}$. By applying this equation to viscosities and using the logarithmic form we obtain

$$\log N = \log No + c\,K \qquad (7)$$

and

$$\log N - \log No = c\,K \qquad (8)$$

which is the same as formula (6).

TABLE IV

K for Naphthalene Solutions

In Benzene		In Toluene	
% Naphthalene	K	% Naphthalene	K
8.11	0.004392	5.73	0.004293
17.16	0.004626	13.72	0.00461
22.97	0.004584	20.12	0.004636
28.82	0.004702	27.31	0.004793
34.10	0.004724	Average for K =	0.004609

TABLE V

Viscosities of Diphenyl Solutions

In Benzene			In Toluene		
% Diphenyl	Viscosity	K	% Diphenyl	Viscosity	K
0	0.6051		0	0.5526	
18.08	0.7585	0.005427	21.38	0.7335	0.005752
30.57	0.9014	0.005662	Average for K =		.005614

The data of "K" for the naphthalene solutions tabulated in Table IV shows good agreement, and the same holds for solutions of diphenyl in benzene and toluene (Table V) the viscosity data of which has also been taken from the work of Kendall and Monroe.

Since the concentration by weight percent has been considered with respect to the relative viscosity, the constant "K" must be a function of the molecular weight

$$K = k.M \qquad (9)$$

and formula (6) becomes

$$\log \text{relat. viscosity} = c.k.M \qquad (10)$$

where "*k*" denotes a universal constant and "*M*" molecular weight. The molecular weights of two different compounds must be in the following ratio:

$$\frac{M_1}{M_2} = \frac{\log \text{rel visc}_1\, c_2}{\log \text{rel visc}_2\, c_1} = \frac{K_1}{K_2} \qquad (11)$$

For diphenyl ($M_1 = 156$) and naphthalene ($M_2 = 128$) the calculations of both sides of the equation give the value 1.2.

The value for "*k*" has been calculated and found

$$k = 3.6 \times 10^{-5}$$

Formula (10) has been tested on different viscosity data of solutions and has been found to be as accurate as the cryoscopic method for determination of molecular weight (Table VI).

TABLE VI

	% By-Wt.	Rel. Visc. @ 25°	k.M	M	M Calculated	Error
Sucrose in water	13.03	1.3083/0.8953	0.01264	342.1	351	+2.6%
Benzyl-benzoate in toluene	41.69	1.183/0.552	0.00794	212.1	220	+3.7%

That the uniformity of the solvent has no influence upon the validity of this method may be seen from viscosity measurements of naphthalene dissolved in mineral oil. The viscosities were taken at 70°C and the mineral oil had an average molecular weight of about 300.

	%	Time of flow in (sec.)	Spec. Gravity	log time of flow + log spec. grav.
Mineral Oil		44.5	0.8473	1.57640
Naphthalene in Mineral Oil	17.3	37.0	0.8514	1.49833

The log relative viscosity would be 0.92193 − 1, a negative figure, which corresponds to a negative value for k. Putting both negative figures in formula (10) and multiplying both sides with −1 we obtain for k.M = .00451, from which a molecular weight of 125.3 for naphthalene is calculated, which differs from the real molecular weight 128.1 by 2.2%.

In cases where the logarithm of the relative viscosity is not a straight line function of the concentration, association and/or solvation may be assumed.

In cases where solvation occurs, the degree of solvation can be calculated from formula (10) assuming that the molecular weight of the solute is known and that the solute is not associated.

$$\log \text{rel. viscosity} = c.f^2.k.M \qquad (12)$$

where "*f*" is the solvation factor by which the concentration and also the molecular weight of the solute has to be multiplied to obtain the concentration which is composed of solute plus solvent.

It is generally accepted that gel formation and high relative viscosities of sols of lyophilic colloids are caused by solvation. If solvation is considered as a chemical combination between solute and solvent or as some form of attachment of the solvent to the dispersed phase, it can only occur in cases where both components are polar. There are however substances which show the same phenomena of colloids in non-polar solvents such as benzene. Hence solvation in this case can be considered as a solution process, which also applies to true solutions. Thus it seems that the term "solvation" is rather an indefinite one in its meaning.

The polar substances present in asphalts are the asphaltenes and asphaltic resins since they form molecular compounds with ferric chloride and mercuric bromide. Since asphaltenes are soluble in asphaltic resins (Sachanen[9]) and from other reasons to be discussed later, both groups were studied from the viewpoint of solvation. The procedure was as follows: 2 g of asphaltenes were shaken for 30 minutes with 1, 2 and 3 g of resins dissolved in petroleum ether to give a final volume of 100 cc. After centrifuging the concentrations were determined. In order that equal particle size of the asphaltenes could be obtained in each case, the asphaltenes (2 g) were dissolved in 10 cc. of benzene and precipitated by slowly adding sufficient petroleum ether to give a total volume of 200 cc. The precipitated asphaltenes were separated by centrifuging for 20 minutes. The liquid was decanted, and the asphaltenes were shaken with 200 cc. of petroleum ether and centrifuged again.

From a consideration of the system "asphaltenes-resins" there are three possibilities: (a) Formation of a chemical compound, the amount of resins combined with the asphaltenes must be constant; (b) solutions of the resins in the asphaltenes; Henry's law of distribution must be obeyed. (c) Adsorption of the resins at the surface of the asphaltenes according to Freundlich's law

$$a/m = Kc^{1/n} \qquad (13)$$

where a = weight of the adsorbed material in g; m = adsorbent in g; K and n = constants.

The data shows that cases "*a*" and "*b*" are not found to hold—

No.	Amt. of resins g	Amt. of asphaltenes g	c_1 Concen'n. of resins in asphaltenes %	c_2 Concen'n. of resins in pet. ether %	c_1/c_2
1	1	2	13.64	0.7420	18.38
2	2	2	21.36	1.6048	13.31
3	3	2	23.77	2.5760	9.22

By the application of Freundlich's law to the results obtained, and by dividing the equations for 2 in 1 and for 3 in 4, the calculated values for 1/n are equal to 0.58 and 0.57, indicating that the resins are adsorbed by the asphaltenes. In 3 the saturation point is almost reached and a further addition of resins would not increase the amount of resins adsorbed by the asphaltenes.

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[9] Petroleum Zeit., **21**, No. 23, 1442 (1925).

Since surface phenomena have a predominating influence it can be assumed that the distribution law is masked by them, and that adsorption is a limited case of solution.

The petrolenes from the Mexican asphalt under investigation represent a solution containing 30.6% of resins and 69.4% of oily constituents. In the asphalt mixture containing 20% of asphaltenes 24.48% of resins are present, and we may assume that in this system also 23.77% of the resins as in 3 are combined with the asphaltenes due to solvation. Since the concentration as well as the molecular weight are both 1.23 times higher when solvation is assumed, the logarithm of the relative viscosity must be 1.51 times higher to conform with formula (12). Taking the logarithm of the relative viscosity at 120°C as base, the corresponding logarithms of the relative viscosity are 1.8 times higher at 37.8°, 2.0 at 25°, 2.12 at 15.5°, and 2.5 times higher at 0°. These values are too high to account for solvation, and it is more reasonable to consider high relative viscosity as a result of association of the molecules of the solute, due to the inability of the solvent to overcome the space lattice forces which cause the polymeric bond.

The data of *k.M* and *M* according to formula (10) for the different solutions of asphaltenes in petrolenes are given in Table VII. It will be readily seen that the asphaltenes are in true solution at 120° and associate with decreasing temperature, and that the degree of association increases to a certain concentration only to decrease again. This is in accord with the fact that polar substances in solution which associate to form chain molecules (the dipole moment is increased) may obtain their highest polarity at a certain concentration, which differs with different temperatures.

The average molecular weight of 1800 for the asphaltenes calculated from the relative viscosities indicates that the asphaltenes must be considered as hemicolloids.

TABLE VII

% Asphalt tenes	k.M	@ 0° M	Degree of Assoc.	k.M	@ 15.5° M	Degree of Assoc.	k.M	@ 25° M	Degree of Assoc.
2	0.16496	4580	$2\frac{1}{2}$	0.1698	4710	$2\frac{2}{3}$	0.1301	3610	2
5	0.1650	4580	$2\frac{1}{2}$	0.1446	4010	$2\frac{1}{4}$	0.12531	3480	2
10	0.1856	5160	3	0.1459	4050	$2\frac{1}{4}$	0.13012	3610	2
16	0.17347	4820	$2\frac{2}{3}$	0.15428	4280	$2\frac{1}{3}$	0.14405	4000	$2\frac{1}{4}$
20	0.16267	4520	$2\frac{1}{2}$	0.13865	3850	$2\frac{1}{8}$	0.12823	3560	2

% Asphalt tenes	k.M	@ 37.8° M	Degree of Assoc.	k.M	@ 120° M
2	0.09553	2650	$1\frac{1}{2}$	0.06568	1820
5	0.09542	2650	$1\frac{1}{2}$	0.0640	1780
10	0.12871	3580	2	0.0635	1760
16	0.12907	3580	2	0.0662	1830
20	0.11753	3260	$1\frac{4}{5}$	0.0652	1810

Average M = 1800

Sachanen[2] determined the molecular weight of asphaltenes in benzene by the cryoscopic method and found values of 5–6000. The molecular weights of the asphaltenes from oxidized Mexican asphalt determined by the same method have been found to be of the same order. However, it was observed in one case that partial separation of the two phases took place. Molecular weights of the same asphaltenes in benzene solution determined by the viscosimetric method yielded the following results (Table VIII). The viscosities were determined at 25° and 7°, the latter in the neighborhood of the freezing point for benzene.

TABLE VIII

Viscosity of Asphaltene solution in Benzene

	%	Time of flow in (sec.)	Spec. Grav.	k.M	M
@ 25°	0	25.1	.8765		
	4.102	45.75	.8852	.0646	1794
@ 7°	0	32.2	.8855		
	4.102	70	.8942	.08324	2312

The molecular weight obtained from the viscosity of the asphaltene solution in benzene at 25° compares favorably with the values given in Table VII. At lower temperature the asphaltenes associate but not to such an extent that molecular weights of 5–6000 can be expected.

Supersaturation

It has already been pointed out that asphaltenes in the dry state cannot be redispersed in the petrolenes. This is readily understood when the average size of the molecules forming the petrolenes are taken into consideration. The molecules are too large to penetrate into the interstices between the asphaltene molecules. The asphaltenes have been found to be soluble in the resins when a solution of both components in benzene is evaporated. However, from a benzene solution of asphaltenes and oily constituents from Mexican asphalt the asphaltenes will settle out after evaporation of the benzene has taken place. In some asphalts the oily constituents are of aromatic structure, and they would therefore keep the asphaltenes in solution under the above conditions.

Since the asphaltenes from the Mexican Asphalt are insoluble in their corresponding oily constituents, it can be said that the asphalt forms a supersaturated solution of asphaltenes.

P. von Weimarn[10] who investigated the relation between particle size and supersaturation gave the following equation:

$$N = J\,P/L \qquad (14)$$

where N = Dispersion coefficient—amount of particles for a given concentration; P = Degree of supersaturation influenced by the diffusion constant *i.e.*

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[10] Alexander's "Colloid Chemistry," 1 (1926).

molecular mass, and is a function of temperature; J = Factor expressed by the velocity of condensation of the solute. This factor varies in the same sense as the actual size of the particles in solution and the viscosity of the solvent. It is also a function of temperature; L = The ordinary solubility of the solute.

It follows that N is extremely great when colloid conditions result. This can be obtained by reduction of the solubility L by increasing P or increasing J.

From this formula it may be expected that the asphaltene particles are smaller when the asphaltenes are insoluble in their corresponding oily constituents.

Investigations made so far have shown that in asphalts which are very susceptible to temperature change, *i.e.*, when the viscosity coefficient increases rapidly with falling temperature, the oily constituents are composed mostly of aromatic hydrocarbons. Since the asphaltenes are soluble in these hydrocarbons, and thus are present in a lower degree of supersaturation, it can be assumed from von Weimarn's equation that the asphaltene particles are larger in size in the case of asphalts, which are less susceptible to temperature change. On the other hand, it may be predicted from their larger particle size that the relative viscosities of very susceptible asphalts are also higher. Unfortunately the work has not been carried through yet with different asphalts from different sources in the way previously outlined. However, the limited data on hand seems to confirm this viewpoint. For comparison the data may be given for an asphalt "*A*" of low susceptibility and an asphalt "*B*" of high susceptibility to temperature change both of the same asphaltene content (Table IX).

TABLE IX

	Asphalt "A"		Asphalt "B"	
Softening Point (Ring and Ball)	64.7°C		64.4°C	
Penetration 100 gr. 5 sec. at 37.8°	100		47	
at 25°	41		16	
Asphaltene content	26.84%		26.97%	
Relative Visc. at 0°	1972		—*	
at 15.5°	1441		29360	
at 25°	544		9206	
at 37.8°	442		1889	
	k M	M	k M	M
k.M and M at 0°	0.1227	3400	—	—
at 15.5°	0.11768	3260	0.1656	4650
at 25°	0.10288	2850	0.1469	4080
at 37.8°	0.09857	2730	0.1214	3370

*This asphalt at 0°C behaved almost as a solid body, so that its viscosity was too great to be measured.

Since we have not yet determined the molecular weight of the asphaltenes from these two asphalts when in the monomeric state, we have to consider the molecular weights in relation to this value at 37.8°C to bring these values to the same basis of comparison. The relations of the molecular weights are:

	Asphalt "A"	Asphalt "B"
@ 0°	1.24	—
@ 15.5°	1.19	1.38
@ 25°	1.04	1.21
@ 37.8°	1.00	1.00

The data seem to be in qualitative agreement with von Weimarn's equation.

Summary

Asphalts have been considered as a sol of asphaltenes in a mixture of asphaltic resins and oily constituents. Viscosity measurements have shown that asphalts have high relative viscosities at lower temperatures only, whereas, in the liquid state they behave like ideal solutions.

Structural viscosity has not been found to occur in the asphalts which have been investigated; it is probable, however, that structural viscosity is more pronounced with higher concentrations of asphaltenes.

An equation has been developed to calculate the molecular weight of the solute from viscosity measurements—log relative viscosity = c.k.M.—where c denotes concentration in weight percent, *k* a constant, and *M* molecular weight.

The application of this equation, together with adsorption measurements of asphaltic resins on asphaltenes, seem to indicate that contrary to general opinion high relative viscosity is brought about by association rather than by solvation.

Von Weimarn's equation dealing with particle size and degree of supersaturation was found to hold qualitatively for asphalts from two different sources which have the same asphaltene content, but show differences with respect to susceptibility to temperature change.

The author desires to express his thanks to the Directors of the Imperial Oil Refineries, Limited, for the privilege of presenting this paper.

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THE SORPTION OF ORGANIC VAPORS BY GLYPTAL RESINS

BY CLARENCE H. WINNING AND JOHN WARREN WILLIAMS

Within the last years considerable progress has been made with studies whose purpose is to elucidate the structure of organic compounds of high molecular weight. The formation of these substances is thought to result from a number of recurring atomic groups which are linked together into large units by primary valence forces. A number of these units may or may not then be associated into larger groups to form what are known as crystallites or micells. Gel substances of this general type exhibit what we understand as colloidal properties. A surprisingly large number of these substances show regularities in the association of chain molecules and of the micells, but others are characterized by the presence of giant molecules arranged with a high degree of randomness. The resin formed by the reaction between glycerol and phthalic acid, technically known as glyptal, seems to be one of the latter type. It is, nevertheless, a porous body, and as such should show a swelling under proper experimental conditions.

There are two general methods for the study of the swelling of a gel. In the first one, the substance is immersed in a liquid and the changes produced in certain of its physical properties are observed. For example, there will be a change in the volume, a change in the power to scatter light, and a change in the refractive index. The other method, commonly known as sorption, consists in allowing the porous body to come to equilibrium with proper vapors. The relationship between the two methods is obvious at the saturation pressure of the vapor.

The work to be reported in this article is a sorption balance study of the equilibrium of glyceryl phthalate resins in the presence of acetone and methyl alcohol vapors. Its objects are five-fold: 1. To determine the form of the sorption isotherms at several temperatures and to interpret the curves in terms of the porous structure of the resin. 2. To determine the heat of the sorption process by the comparison of two isotherms. 3. To make an estimate of the average pore size from the sorption behavior in the neighborhood of saturation. 4. To study the changes in structure produced by variations in the curing process to which the resin has been subjected. 5. To study the reversibility of the sorption process.

So little is known regarding the structure of a synthetic resin that several kinds of investigation likely to contribute to the ultimate interpretation should be made. Experiments of the type to be reported here at least make possible a basis for the scientific comparison of different resins. It is also believed that when sufficient data can be accumulated the method will be successful in demonstrating the existence and type of micellar structure. To obtain an estimate of the dimensions of these micells it will probably be necessary to combine these results with deductions from other even more physical lines of reasoning such as a study of the elastic properties of the gel and the dielectric constant relations of proper suspensions in liquid media. Data of this sort should be of considerable value to industries interested in the development of these and other substances as plastics and varnishes, because among other things they will contribute to an understanding of such properties as the rigidity of the resins, and the retention of vapors by them.

Experimental

Apparatus and Procedure. The experimental results to be presented are sorption and desorption isotherms of glyptal resins in equilibrium with different vapor pressures of acetone and methyl alcohol.

The apparatus used was a McBain-Bakr balance,[1] adapted to the sorption of vapors by powdered resins. In principle it is a spring balance suspended in an evacuated chamber. The required vapor pressure of the organic liquid was obtained by maintaining a known temperature in a bath surrounding the liquid which had been collected in the reservoir, which is in turn connected to the sorption chamber proper. The amount of sorption at any vapor pressure was obtained from the difference in weight, determined from the elongation of the spiral, between the sample before and after the sorption process had taken place.

The procedure will be evident from a study of Fig. A, in which the apparatus is diagrammed. The four quartz springs were suspended from brass cylinders which were mounted in the special sorption chambers. The ground glass joints fitted with mercury seals facilitated the changing of samples. The chambers containing the springs were maintained in a well-insulated air thermostat fitted with double plate glass windows on opposite sides. The temperature in the bath was controlled by a special mercury-toluene regulator which permitted variations not greater than 0.2°C.

Evacuation of the system was accomplished by means of a mercury vapor condensation pump backed by an oil pump of conventional design. Oil vapors were prevented from entering the vacuum line and organic vapors were prevented from reaching the pump by means of liquid air traps. The pressures were indicated by a McLeod gauge.

After thorough evacuation of the system to remove moisture the liquid whose vapors are to be sorbed is introduced into a side tube J—connected with the main sorption chamber by a capillary tube. The liquid was then frozen with liquid air and the system again evacuated. As the solidified liquid was allowed to warm up and melt, any gases which had been dissolved were given up. The liquid was again frozen and the system re-evacuated. This process of outgassing the liquid and evacuation was repeated until the dissolved gases had been completely removed.

The lengths of the quartz springs were then measured to obtain the weight of the dry resin samples in vacuo. These samples are contained in extremely

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[1] J. Am. Chem. Soc., 48, 690 (1926).

thin glass bulbs fitted with hooks to attach them to the spirals. Each balance had been previously calibrated throughout the working range by noting the elongations caused by known weights, using a precision cathetometer which was accurate to 0.01 mm. Within the limits of error and within the range in which we were operating the elongations produced over successive 0.05 g. intervals could be considered to be proportional to the weights attached. Previous to the calibration the springs had been carefully annealed.

The liquid was then distilled at a low vapor pressure from the side tube through the capillary tubes connecting tubes *I* into the bottoms of the liquid retaining tubes *H*. Condensation on and sorption by the samples was prevented by chilling the bottom of these tubes with liquid air contained in vacuum bottles. After a sufficient amount of the organic vapor has been condensed each of the four units is sealed off at the constricted connecting tube.

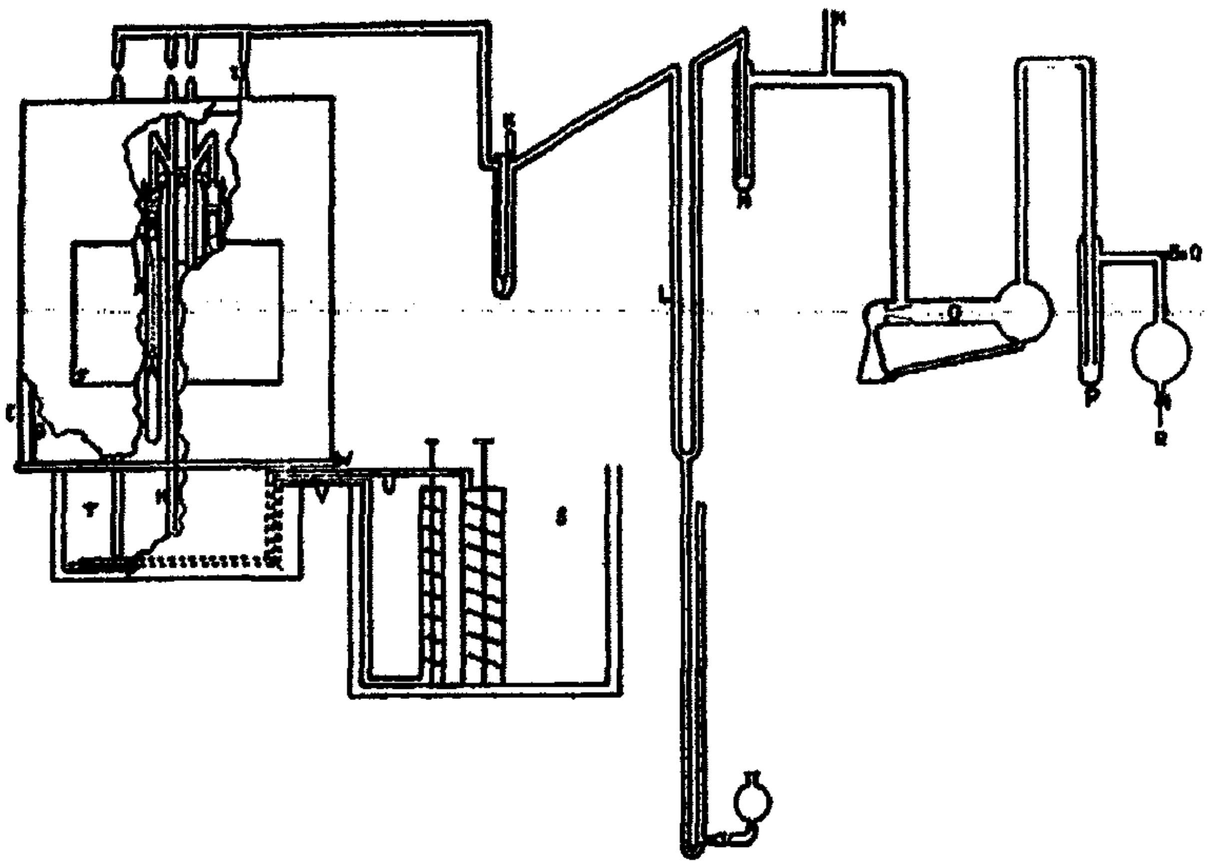

FIG. A
Diagram of Apparatus

To control the vapor pressure of the liquid in the sorption chambers it was necessary to circulate a liquid at controlled temperatures about the portion of the tubes in which the liquid was contained. Since it was at times necessary to cool the liquid to temperatures below zero it was convenient to use a mixture of glycerine and water for this purpose. It was pumped from a thermostat in which the temperature was regulated to 0.02° C. The circulation was such that at least 6 liters of the thermostat liquid flowed in each direction in 1 minute. The corresponding vapor pressure of the sorbate was obtained from standard tables of physical constants. Measurements of the elongation of the spiral were always continued until no change in the reading of the cathetometer could be observed after a 4 hour period. It was then assumed that the sample had reached a constant weight. That this assumption was not always entirely justified will be evident from a study of the sorption curves in the regions of low vapor pressure. It happens, however, that the very slow rate of sorption in these cases is of considerable importance for the conclusions with regard to the structure of the resin, and they will be considered in some detail. Constant weight was never attained in less than 24 hours, and sometimes considerably longer periods of time were required. The amount of sorption at any of the pressures used could always be calculated from the weight of the dry sample in vacuum. For each sample at a given temperature both sorption and desorption curves were obtained. The pressures ranged from very small values to values approaching saturation. This method of experimentation has the advantage that in addition to the equilibrium value itself the rate at which the sorption equilibrium is attained may be observed.

The sorption took place in samples of resin which had been prepared in powdered form. The adsorption on the external surface of the powder was of minor importance compared to the process taking place within the structure of the resin itself.

Materials used. The acetone was purified by distillation from the sodium iodide addition product, and subsequent drying, following the directions given by Shipsey and Werner.[2]

Methyl alcohol of a high grade of purity was subjected to the treatment described by Bjerrum and Zechmeister[3] for the removal of water.

The glyptal resin samples were prepared using glycerol (98% grade) and phthalic anhydride (C.P. grade). The relative proportions of these substances used was two molecules of glycerol to three molecules of phthalic anhydride. The glycerol was first heated to 200° C, then the anhydride was added, taking care to always maintain this temperature during the course of the reaction. The reacting mixture was frequently stirred. The heating was continued for exactly four hours. Samples of this resin were cured in an oven maintained at 105° C for periods of time up to 275 hours. All resin samples, unless otherwise noted, were taken from the same parent resin and cured for the lengths of time indicated in the tables of data, and in the discussion of the solubility of the resins.

A cellulose acetate sample was obtained from the Eastman Kodak Company. It was described by them as having been prepared by a method which "leads to the complete solution of the cellulose acetate in the esterifying bath."

Data and Results

Data and Graphs for the Sorption Isotherms. The experimental data are presented in the form of tables and graphs. In each case the number assigned to the graph corresponds to the number of the table. The data of Table I have been plotted on three curves. The first graph shows the position of the sorption and desorption isotherms at 50° for acetone vapor on the several samples of glyptal resin. Recognizing the fact that the sorption and desorption processes were so slow in the region of the very low relative pressures that it would be quite impossible in the time at our disposal to attain the true

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[2] J. Chem. Soc., 103, 1255 (1913).

[3] Ber., 56, 894 (1923).

equilibrium positions of the isotherms, we have plotted a second series of isotherms which have been called equilibrium curves. These curves have been obtained by an averaging process from the sorption and desorption curves as actually observed. In assigning an x/m value for a given p_x/p_s the relative rates of the sorption and desorption processes have been considered. For the more nearly reversible systems (the cured resins) the greater portion of the equilibrium curve could be calculated without much difficulty, and, we believe, with considerable accuracy. It is of course true that there is a considerable uncertainty in the position of the equilibrium isotherms at the very low relative pressures. It may be well to remark at this point that what conclusions we have drawn from the first portions of the various isotherms in the sections of this report have depended not upon the position of an equilibrium curve but upon the rate at which progress toward such an equilibrium was being made. These equilibrium curves are shown in Fig. 1a.

Fig. 1b, for which data are found in Table I as well as in Table Ib, shows the 35° and 50° isotherms for acetone vapor being taken up by the sample of cellulose acetate. It will be observed that the hysteresis is somewhat less at the higher temperature. The points on the curves have been obtained only after at least 24 hours was allowed for the attainment of equilibrium. Even under these conditions there was some evidence that the true equilibrium position had not been attained, in spite of the fact that several recent investigators claim that other vapors come to equilibrium with this and similar material in periods of one and two hours. We should also mention that all of our experiments have been made in a continuous manner, the relative satura-

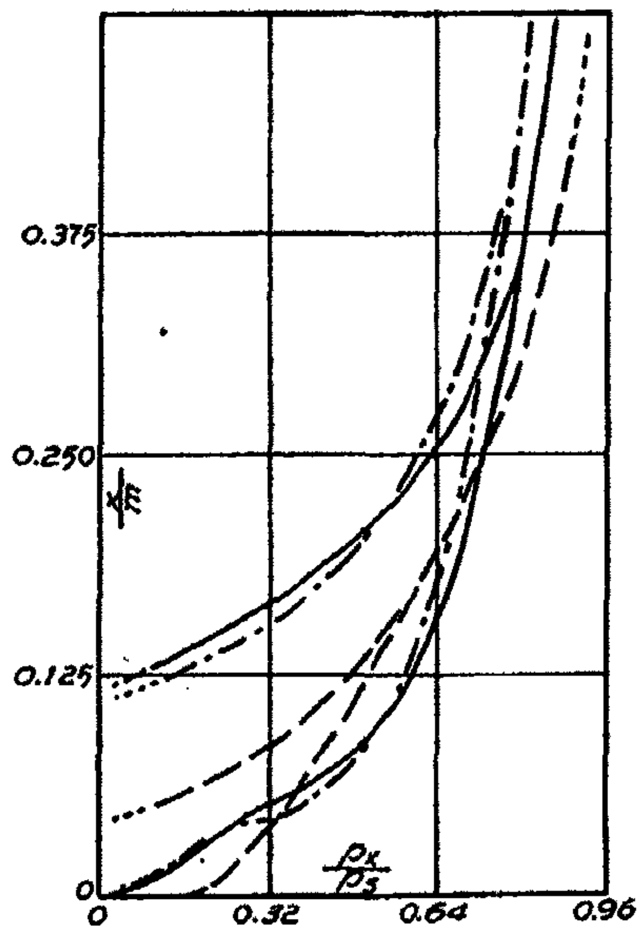

FIG. 1

Acetone—50° Isotherms
— — — Special Resin
——— Resin I
— — Resin III

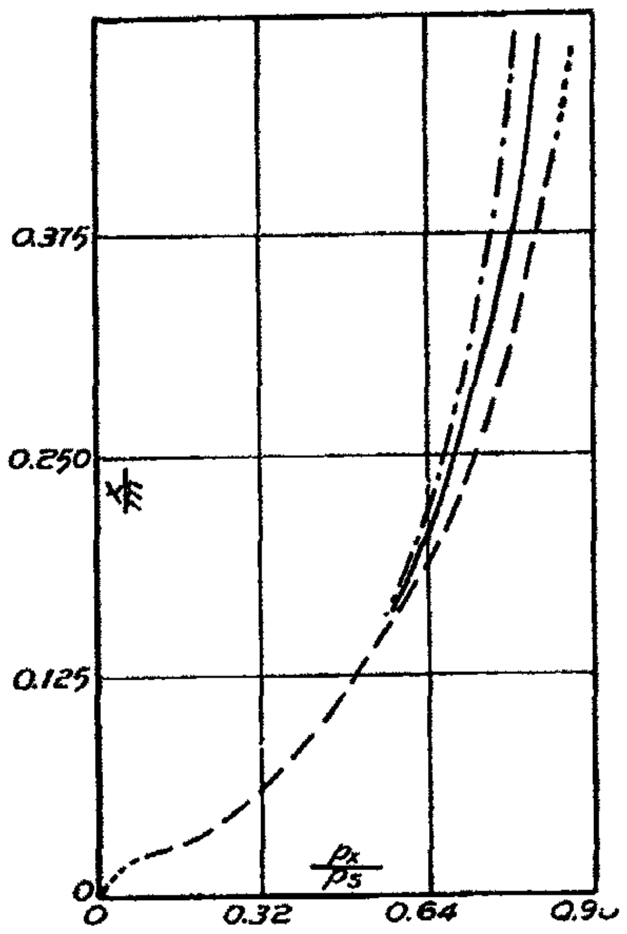

FIG. 1a

Acetone—50° Isotherms
Equilibrium Curves

tion pressures being gradually increased, and, after reaching a practical limiting value, they were gradually reduced, with stops of not less than 24 hours at pressures where observations were made.

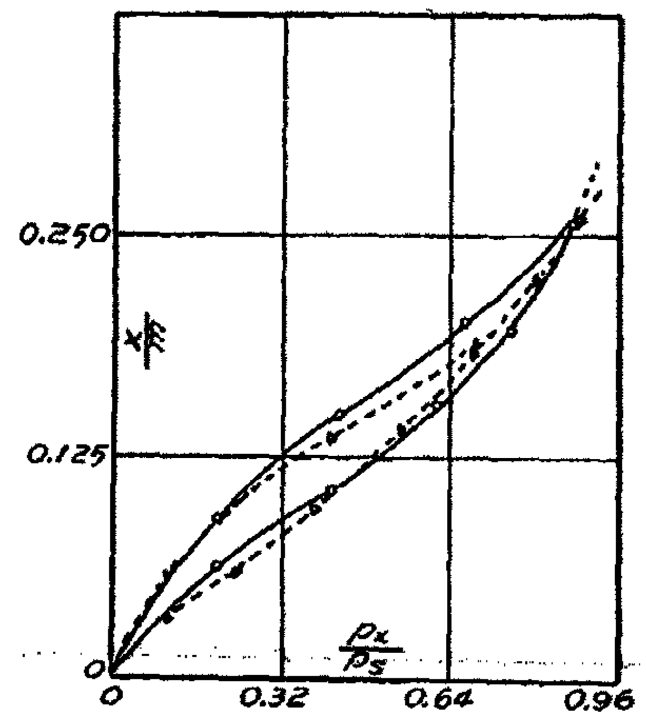

FIG. 1b

Acetone—Isotherms for Cellulose Acetate

------ 50° Curve

——— 35° Curve

TABLE I

Data for 50° Isotherms—Acetone Vapor

p_x/p_s	Amount sorbed per Gram (x/m) Resin I[*]	Special Resin[**]	Resin III	Cellulose Acetate
0.109	0.011	0.011	0.000	0.035
.230	.033	.034	.007	.060
.374	.059	.043	.057	.096
.543	.097	.101	.141	.141
.687	.206	.236	.215	.185
.804	.378	.465	.308	.228
.882	.560	.670	.408	.261
.687	.273	.304	.222	.190
.408	.185	.173	.102	.136
.109	.130	.120	.050	.057

[*] In this and the following tables, as well as in the text, Resin I refers to a sample of glyptal resin prepared by cooking for exactly 4 hours, which is uncured; Resin II refers to samples of the same resin which have been cured for 42 hours; and Resin III refers to similar samples which have been cured for 275 hours.

[**] This resin differs from Resin I in that it was removed from the reaction flask at the end of a 3 hour period.

TABLE Ib

Data for 35° Isotherms—Acetone Vapor

Cellulose Acetate			
p_x/p_s	x/m	p_x/p_s	x/m
0.193	0.063	0.871	0.258
.407	.106	.662	.201
.608	.155	.424	.149
.752	.197	.193	.090

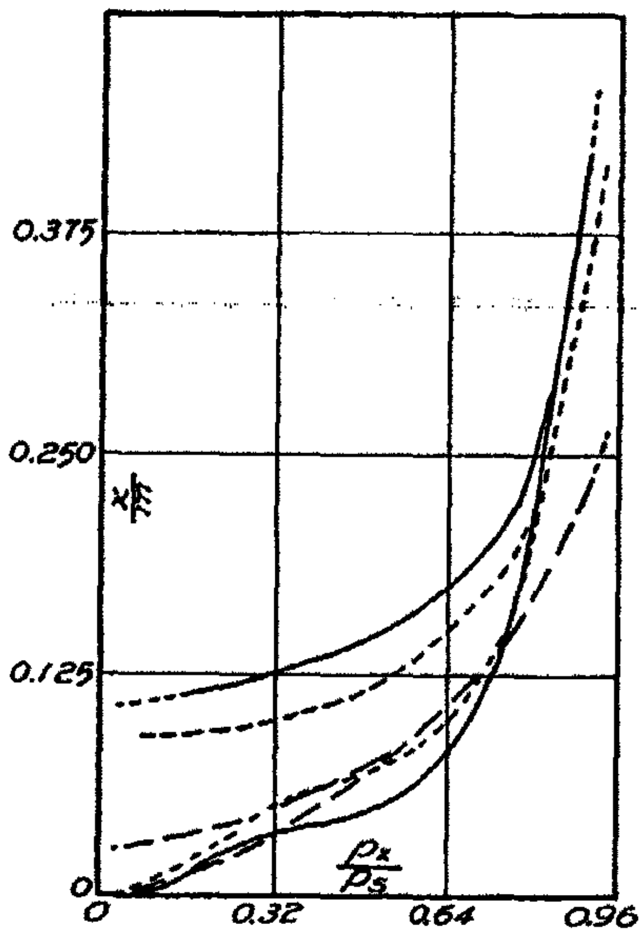

FIG. 2

Methyl Alcohol—50° Isotherms

——— Resin I

------ Resin II

— — Resin III

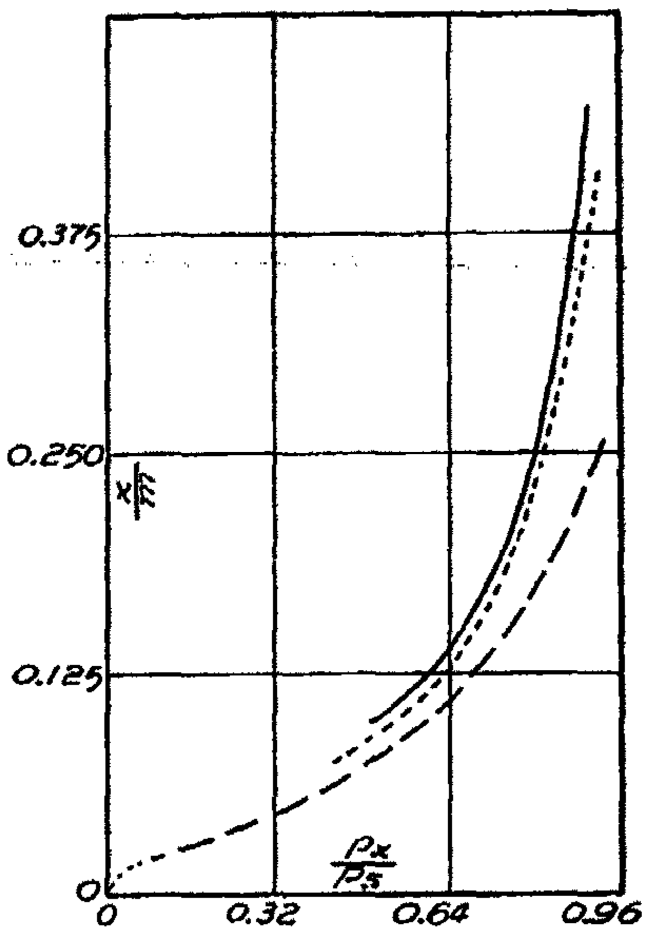

FIG. 2a

Methyl Alcohol—50° Isotherms

Equilibrium Curves

Table II and Figs. 2 and 2a have been constructed from the experimental data taken during the 50° sorption and desorption process for resins in the presence of methyl alcohol vapor. The figures correspond to those just presented for the behavior of the resins in the presence of acetone vapor.

In order to be able to compare directly the difference in behavior between acetone and methyl alcohol with respect to a given resin Table III and Fig. 3 have been presented. They show that although the affinity of the resin for acetone is greater than it is for methyl alcohol, the rate at which the methyl alcohol is able to penetrate the resin at the beginning of the sorption process is the greater.

TABLE II

Data for 50° Isotherms—Methyl Alcohol Vapor

Amount sorbed per Gram (x/m)

p_x/p_s	Resin I	Resin II	Resin III	Cellulose Acetate
0.073	0.002	0.005	0.007	0.014
.265	.031	.041	.026	.038
.456	.044	.067	.062	.060
.748	.148	.155	.143	.102
.898	.408	.344	.228	.134
.762	.220	.195	.149	.120
.476	.146	.116	.072	.079
.167	.115	....	....	....
.073	....	.093	.029	.014

TABLE III

Data for 35° Isotherm

Methyl Alcohol Vapor

Resin II

p_x/p_s	x/m
0.147	0.010
.355	.035
.559	.081
.760	.124
.910	.252
.708	.174
.430	.132
.430	.087

Data for 35° Isotherm

Acetone Vapor

Resin II

p_x/p_s	x/m
0.193	0.005
.288	.016
.425	.071
.582	.130
.794	.338
.648	.238
.467	.195
.256	.183

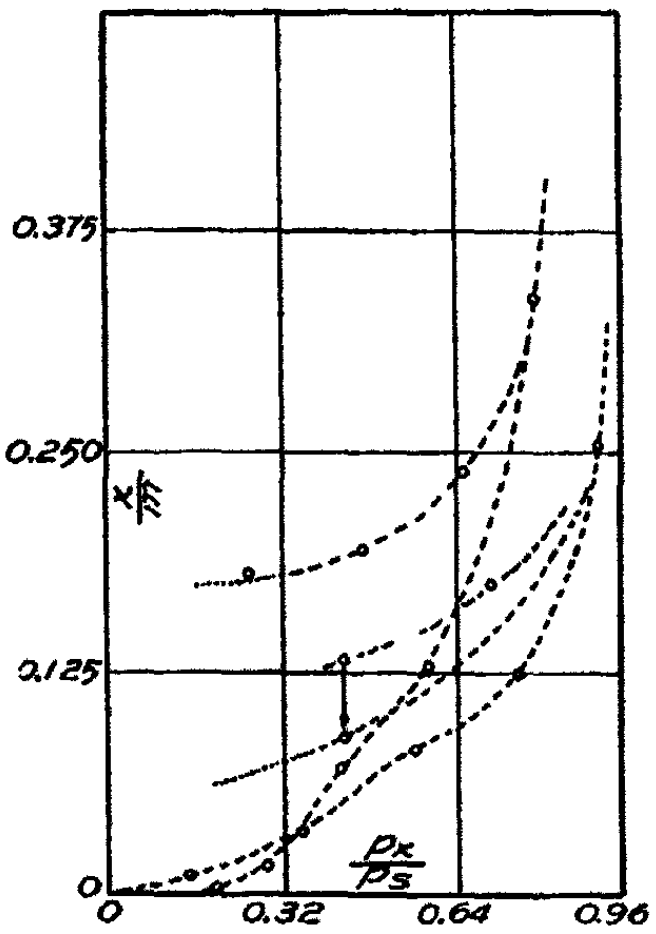

FIG. 3
Resin II—35° Isotherms
Upper Curve—Acetone
Lower Curve—Methyl Alcohol

The data of the three tables represent approximately one-half of the experimental measurements. The other data, obtained for the most part at 35°, are in all respects similar in character, and have not been published solely in the interest of a saving in space.

Solubility of the Resins in Acetone and Methyl Alcohol. Approximately 0.1 g samples of each of the series of resins were covered in test tubes with 5 to 6 cc of dry solvent. The tubes were then sealed. The solvent action was followed for a considerable period of time. The tubes were viewed by both transmitted and reflected light, and in a Tyndall beam. The results of these solubility tests, using acetone and methyl alcohol as solvents, are tabulated below. The word "solution" is used in the sense in which it is usually applied to materials of this sort. The resins used were of the series previously described in the section on the purification and preparation of materials.

Acetone as Solvent

Resin cooked 3 hours.—Immediately soluble to give a clear liquid. Shows faint Tyndall beam.

Resin cooked 4 hours (Resin I).—Immediately soluble to give a clear liquid. Shows Tyndall beam.

Resin II. (Resin I cured 42 hours).—Apparently insoluble. Liquid gives Tyndall beam. Solutions appear clear to ordinary observation. Insoluble gummy residue.

Resin III. (Resin I cured 275 hours).—Very faint Tyndall beam. Residue in powdered form.

Cellulose acetate.—Gives clear solution that exhibits Tyndall beam.

Methyl Alcohol as Solvent

Resin cooked 3/4 hour.—Dissolves in a few hours. Solution is slightly cloudy. Cloudiness later disappears and a slight precipitation is visible on the walls of the tube. Very faint Tyndall beam.

Resin cooked 2 1/2 hours.—Partly dispersed in solution to give cloudy suspension, which later settles out on walls of tube. Very faint Tyndall beam. Insoluble portion at bottom is transparent gummy mass.

Resin cooked 3 hours.—Slight Tyndall beam. Solution appears clear to ordinary observation. Less sedimentation on walls than for previous resins. A transparent residue of insoluble resin remains.

Resin I.—Gives clear solution which shows slight Tyndall effect. There is also transparent and insoluble residue left in the bottom of the tube.

Resin II.—Gives clear solution which shows faint Tyndall effect. Transparent and gummy residue remains.

Resin III.—Gives a clear liquid which shows no Tyndall effect. Residue appears as it did when dry.

Cellulose Acetate.—Gives no evidence of solubility.

The condition of the samples in the various tubes containing acetone and methyl alcohol after they had been kept in an oven at 105° was apparently unchanged after one week.

These data show that acetone is a much better solvent for the resins than methyl alcohol.

Discussion of Results

The sorption of vapors by gels of the swelling or elastic type and the resultant volume change has been the subject of many investigations. The amount of vapor which may be taken up by them and the degree and manner in which they swell are undoubtedly related to their chemical and physical structures, yet data of the type presented above without other evidence probably can never give a completely satisfactory means to describe them. It is well known that different gels swell to varying degrees up to the extreme case where a kind of solution of the solid body is effected through resolution into the constituent micells or other structural units. Where such a solution has been formed it seems clear that a sorption process is no longer involved, but in the intermediate cases it is not readily possible to say where one process has been completed and the other has begun. But even in spite of such difficulties one can readily justify sorption studies on substances of the sort considered here in terms of the information which is made available by them.

A number of theories have been proposed to describe the structure of resins as highly polymerized organic substances. For purposes of discussion we shall classify them as gels, since it is more or less tacitly agreed that they are heterogeneous in the sense that there is present both a continuous and a disperse phase, with the two phases forming a network. The structure of highly polymerized organic substances is usually interpreted on the assumption that the disperse phase is made up of simple molecular units which have aggregated to form micells. In some cases these micells are now known to be arranged according to a regular pattern while in others it is supposed that the arrangement is a random one. In the case of the glyptal resins the existence of building units of the micellar type has not, as far as we are aware, been demonstrated. Also in some ways it does not seem logical to assume their existence, rather it is advantageous to consider the most important structural units to be giant molecules. It is of course true that these giant molecules may associate with each other in a way which is similar to the dipole association of liquids like water and alcohol, forming units which might be compared to micells, but they will be the result of chance aggregations and will not result in any regular arrangements.

One may even go so far as to predict that when molecular size and molecular weight determinations with any particular sample of glyptal resin can be made the units will be found to be monodisperse, a result similar to that which has already been found by Svedberg and his associates for a number of the proteins. To start the resin formation 1 molecule of glycerol may be assumed to react with 3 dibasic acid molecules. This substance may then combine with 3 more glycerol molecules and the process might be considered to be an endless one, with the chains becoming more and more branched as new glycerol molecules take part in the reaction. But the results of recent molecular structure studies teach that there is a certain freedom of rotation of groups about single valence bonds and that the angles made by the valence bonds attached to the carbon and oxygen atoms remain sensibly constant in compounds. Therefore it may be expected that the reaction will eventually be retarded due to inner esterifications leading to the formation of closed rings.

The sorption of vapors by such a system will be a slow process because the molecules of the sorbate will have to penetrate between and around the giant molecules. This process should therefore depend to a large extent upon the size and polarity of the vapor molecules. The strong cohesive forces holding the larger units to form the solid material will have to be overcome so that there must be an actual attraction between sorbent and sorbate for the permeation of the solid mass. Then the structure will be progressively opened up through the continuation of this process which results in the attachment of solvent molecules over the surface of the structural units. The complete solution of the resin may be accomplished in the case of certain liquids through the complete resolution of the solid into these constituent units. It seems likely that in such cases a considerable amount of liquid will be held by capillary forces in the regions between the giant molecules which have now been released from any elastic strain. The vapor molecules will be increasingly sorbed as their relative pressures become higher and higher.

Form of Sorption Isotherms. The equilibrium sorption isotherms of swelling gels are typically "S" shaped. The sorption isotherms for cellulose acetate which we have determined show this behavior very nicely but our isotherms for the glyptal resins do not entirely conform. We are confident that the reason for this condition is due to our failure to realize the true equilibrium at the very low relative vapor pressures, rather than to any failure of the resin to conform to the general behavior. The form of our sorption isotherm is shown by the full line of Fig. 4. There has also been indicated by broken line the probable equilibrium position of the isotherm. The structure of the resin is so extremely fine that such gases as hydrogen and oxygen pass through thin films only with the greatest difficulty. The penetration by larger molecules such as methyl alcohol and acetone vapors will therefore be very slow even in the evacuated sorption chamber and true equilibrium can be attained only after very long periods of time.

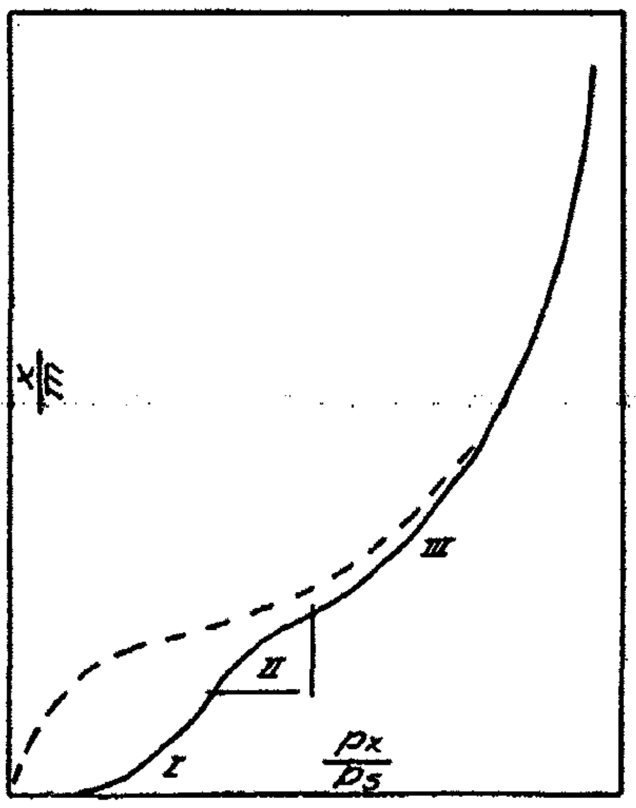

Fig. 4

Schematic Diagram of Sorption Curve
———— Observed Curve
— — — — Equilibrium Curve

For purposes of discussion the typical isotherm will be divided into three regions. In the first of these regions it may be said that the giant molecules are held together by strong cohesive forces which are eventually overcome by the highly polar sorbate molecules. An inspection of the experimental data, and a study of the rate at which the vapors are sorbed show that these cohesive forces have increased in strength as the curing time of the resin is increased. At the same time the sorption tendency or adhesional affinity is correspondingly decreased. The sorption and desorption curves may not coincide, because the reaggregation process is not a reversible one, but it seems more probable that the true equilibrium conditions have not been attained.

Once the sorbate molecules have penetrated the structure of the resin the equilibrium value for the amount adsorbed is attained much more readily. This is indicated by the change in the slope of the isotherm in passing from the first region to the second one. It seems probable that by the time the relative vapor pressures corresponding to the second region have been reached a film of definite thickness has been formed between all giant molecules, and about the branches and rings of these units, in spite of the fact that the sorption and desorption curves are not entirely reversible. The region in which the isotherm becomes parallel to the pressure axis corresponds to the completion of the process which began in region I.

As the external vapor pressure is increased to values corresponding to the beginning of the last region it seems logical to assume that the giant molecules become separated to such an extent that the voids become inter-connecting to form capillaries. The liquid will be condensed in these capillaries and held there at a reduced vapor pressure because of the curvature at the surface. As the sorption continues these capillary spaces fill up and at the same time extend in dimension. The resin takes up considerable quantities of either acetone or methyl alcohol until the saturation value at a given relative pressure is reached, this process being a reversible one practically throughout this third region. It does depend somewhat upon the treatment to which the resin has been subjected in its preparation. This indicates that the gel returns to the same packed condition as the vapors are removed from the capillaries which have been formed in the swelling process.

Thermodynamics of the Process. The results of the experiments are thus explained by assuming a model in which giant molecules are the structural units and in which the process of adsorption (Regions I and II) is followed by one of condensation (Region III). A consideration of the thermodynamics of the process provides ample justification for the division into adsorption regions and a condensation region. If, as has been done in the introduction, it is possible to compare the sorption of vapors with the process of wetting, it can be shown that when one mol of the liquid sorbate, of molecular weight M, is transferred isothermally to the adsorbent which has already adsorbed x/M mols per g, the free energy change in the process is given by the expression

$$-\Delta F = RT \ln p_s/p_x$$

where $-\Delta F$ is the free energy change when the amount x is adsorbed, p_x is the equilibrium pressure above the sorbent when the amount x is adsorbed, p_s is the saturation pressure, R is the gas constant, and T is the absolute temperature. Using the data of an equilibrium isotherm and this expression there can be calculated the change in free energy as the amount adsorbed, x, is increased. As would be expected the values are highest at the beginning of the process, but as the relative saturation pressures increase the values become smaller and smaller.

Values for the decrease in free energy of the 50° and 35° sorption of acetone vapors on the resin sample which had been cured 275 hours are given in Table IV. In the first and second columns there are tabulated observed and equilibrium values of x/m for corresponding values of the relative saturation pressures, p_x/p_s. These data are chosen as typical.

TABLE IV

Free Energy of Sorption Process

50° Isotherm x/m Ads.	Acetone Vapor x/m Equil.	p_x/p_s	Resin III $-\Delta F$ Cal.
0.000	0.025	.1	1478.
.002	.034	.2	1033.
.029	.054	.3	774.
.067	.085	.4	585.
.115	.125	.5	446.
.168	.168	.6	328.
.227	.225	.7	230.
.309	.308	.8	146.
.448	.448	.9	67.
35° Isotherm	Acetone Vapor		Resin III
0.000	0.047	.1	1409.
.000	.051	.2	984.
.005	.064	.3	737.
.032	.085	.4	561.
.092	.120	.5	424.
.165	.165	.6	312.
.217	.216	.7	219.
.320	.327	.8	136.

The change in heat content for the process, $-\Delta H$, may be obtained from the free energy change and its temperature coefficient, using the Gibbs-Helmholtz equation.

$$\Delta H = \Delta F - T\left(\frac{\partial \Delta F}{\partial T}\right)_p$$

$$= RT^2\frac{\partial \ln p_x}{\partial T} - RT^2\frac{\partial \ln p_s}{\partial T}$$

The first term on the right side of this equation will be recognized as the differential heat of adsorption, while the second term, which is quite independent of the amount adsorbed, is the molal heat of vaporization of the liquid being adsorbed. This equation may be written in integrated form for use as follows:

$$-\Delta H = \frac{2.3\ R\ T_1 \cdot T_2}{T_2 - T_1}\left(\log\frac{p_{x_2}}{p_{x_1}} - \log\frac{p_{s_2}}{p_{s_1}}\right)$$

Having determined the equilibrium positions of two isotherms (35° and 50°) it is possible to calculate the differential heats of adsorption for the several systems studied as the amount of vapor adsorbed is increased. It is found in every case that this quantity decreases to a value which becomes constant as the amount of vapor adsorbed reaches the value which marks the beginning of the third and last sorption region. Further, this value is constant for the glyptal resins which have been given different treatments in preparation as long as a single kind of sorbate molecule is involved, and is, within the limits of experimental error, equal to the molal heat of vaporization of that substance. In other words the adsorption has been completed when the third region of the process is reached and it is followed by a condensation in the capillaries which have been formed by the uncoupling of the residual valence forces which held the structural units together. Typical results of calculations for the differential heats of sorption are given in Table V.

TABLE V

Differential Heats of Sorption

Resin III Equilibrium Pressures			Acetone Vapor
35°	50°	x/m	Heat of Sorption per Gram Mol of Acetone
41.6 m.m.	159.3 m.m.	0.045	305. cal.
62.3	173.3	.050	232.
102.5	200.9	.062	153.
123.3	225.4	.075	137.
153.8	269.5	.100	127.
176.7	306.3	.125	125.
213.4	374.9	.175	128.
240.4	428.8	.225	131.
262.6	469.3	.275	132.
276.1	499.9	.325	135.
291.0	524.4	.375	134.
302.8	544.0	.425	133.
Resin III		Methyl Alcohol Vapor	
109.0	202.0	.075	254.*
127.0	245.0	.100	270.
141.0	279.5	.125	280.
153.0	304.0	.150	282.
171.0	343.0	.200	286.
184.0	370.0	.250	287.
192.3	385.5	.287	286.

* The values at the lower relative saturation pressures are in error due to greater difficulty in properly locating the equilibrium isotherms for methyl alcohol for which fewer data are available.

The molal latent heats of vaporization for the two liquids have been calculated from the vapor pressure data. At corresponding temperatures the values are approximately 130 calories and 285 calories, respectively.*

Estimation of Pore Size. One of the primary objects of this research was to make information available concerning the porosity of these resins. Sorp-

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* Sheppard and Newsome (J. Phys. Chem., 36, 930 (1932)) have recently treated data for the sorption of water vapor by cellulose acetate films in a similar manner.

tion studies seem always to receive consideration for such a task, the reason being that in certain quarters it is believed that all material sorbed by a porous body is liquid condensed in its capillaries. Although we do not care to defend this viewpoint, we do feel that the application of the Kelvin relation between capillarity and vapor pressure to our data will permit an estimation of the size of the intermolecular capillaries, especially in the regions of the higher relative pressures. The results of our calculations are intended to indicate an order of magnitude rather than an exact value. From the discussion given above we should have to conclude that the capillary process ceases to be operative for the smaller vapor pressures, so that the smaller values are probably considerably in error.

The Kelvin equation is

$$\mathrm{RT}\ln\frac{\mathrm{p_s}}{\mathrm{p_x}} = \frac{2\sigma}{\mathrm{r}}\cdot\frac{\mathrm{M}}{\mathrm{d}}$$

$$\text{or } \mathrm{r} = \frac{2\sigma\mathrm{M}}{\mathrm{dRT}\ln \mathrm{p_s/p_x}},$$

where p_s is the vapor pressure above a plane surface, p_x is the vapor pressure above the meniscus, σ is the surface tension of the liquid being condensed, M is its molecular weight, d is its density and r is the radius of the capillaries, which are considered to be cylindrical.

Using the data for the 35° isotherms for acetone being sorbed by the several samples of glyptal resin, the following results are obtained. It is assumed that the process of capillary condensation begins where $\mathrm{p_x/p_s} = 0.1$. The data for the tables are taken from the extrapolated equilibrium curves.

TABLE VI

Values for Radius of Capillaries (Acetone)

$\mathrm{p_x/p_s}$	$\mathrm{r} \times 10^8$ cm.	Special Resin* x/m	Resin I x/m	Resin III x/m
.1	5.	—	—	.025
.44	14.	—	—	.100
.56	20.	.158	.154	.150
.72	35.	.312	.280	.237
.80	50.	.450	.375	.307
.84	66.	—	.437	.353

* This resin differs from Resin I in that the 200° reaction between glycerol and phthalic acid was stopped at the end of a 3-hour, instead of 4-hour period.

In the following table a corresponding set of data and calculated quantities are tabulated for a series of resins, the sorbate being methyl alcohol.

TABLE VII

Values for Radius of Capillaries (Methyl Alcohol)

p^x/p_s	$r \times 10^8$ cm.	Resin I x/m	Resin II x/m	Resin III x/m
.1	3.	—	—	.017
.44	8.	—	.075	.062
.56	11.	.112	.100	.087
.72	19.	.176	.162	.135
.80	27.	.237	.220	.170
.88	36.	.370	.322	.214

These values are typical of the results obtained either with acetone or with methyl alcohol. The use of the Kelvin equation can be justified if each molecule of the condensed liquid is surrounded by like molecules, without the sphere of influence of the molecules forming the capillary walls. It is evident, then, that values as small as 3×10^{-8} cm for the effective radii can be of little significance because the molecules of the sorbed material would then have to be in contact with the solid sorbent. The values corresponding to higher x/m values are of what seems to be a proper order of magnitude.

Inspection of these tables seems to indicate that the structural units of the resin become larger as the curing process is continued. For a given relative saturation pressure, and therefore for a given capillary radius, the amount of vapor which is condensed decreases as the length of the curing process is increased. To explain this it seems necessary to assume that the number of these capillaries is greater for the less mature resins, which would indicate the presence of a larger number of smaller molecules. A study of the mechanical properties of the resin suggests that the increase in the size of the giant molecules is probably a lengthening of the irregular chains. This point will be discussed further in the next section where the effect of the curing process over the whole range of the sorption is considered.

Effect of Curing Process. The formation of a glyptal resin may be thought of as occurring in several stages of which we shall mention but two. The first is the rather high temperature reaction between glycerol and phthalic acid in which water is eliminated. If the reaction has been stopped at the proper time a hard, brittle substance is formed on cooling. A second stage of the reaction is the curing process in which this hard brittle substance is heated to approximately 105° over extended periods of time. Although practically no more water is now eliminated the resin undergoes a very pronounced change, because after from 10 to 14 days at this temperature it has become extremely tough and more resistant to solvents. In this condition it will withstand sudden shocks and may be machined quite readily. It seemed of interest to compare the relative abilities of the cured and uncured resins to take up and give off organic vapors to see if any differences in behavior might be interpretable in terms of the respective structures.

The relative positions of the several sorption isotherms indicates that as the curing process is continued the structure becomes more firmly knit together.

The uncured resin takes up the vapors more readily than either of the cured resins. Its isotherm rises quite sharply at the beginning of the sorption while the amounts of vapor taken up by the cured resins are exceedingly small over the same pressure range. The filming process or saturation of the structural units is completed at relatively lower vapor pressures in the case of the more immature resins. Since in these portions of the isotherms the natural cohesive forces holding the resin together must be overcome by the mutual attraction between sorbent and sorbate it is evident that it is becoming more and more difficult for the sorbate molecules to penetrate. The rather large differences in the sorption isotherms for the various resins in the lower parts of the curve show that the physical and chemical structure is profoundly changed by the curing process.

In the second region of the sorption curves, the amount adsorbed at the "saturation value" varies with the particular resin sample. The exact significance of this variation is difficult to determine, because it occurs in a region which is intermediate between two others where the processes of sorption are distinctly different. The former region is characterized by a process probably more chemical in nature, while the latter region is characterized by a process undoubtedly more physical in nature. The definite appearance of an intermediate region in the sorption isotherms must depend upon the fact that this region represents the first real approach to equilibrium in the sorption process. After the process taking place in this region is completed, the resin molecules are considered to be separated by a film of sorbate molecules, so that any available spaces between the closely packed giant molecules now have become interconnecting.

At this point there is a sharp rise in the sorption curve, the beginning of our third region. The point of inflection in the curve is quite pronounced. For the less mature resins this point of inflection is reached at lower vapor pressures. This may be interpreted to mean that the process of capillary condensation begins at lower vapor pressures for these less mature resins, because a greater number of smaller interconnecting capillaries have been formed, making it possible for larger amounts of the condensed vapors to be held at the lower relative pressures. We may conclude that the less mature resins have smaller structural units, for such a structural system would furnish a larger volume of small capillary spaces. A greater number of the smaller capillaries also accounts for the greater steepness of the sorption isotherms for the less mature resins.

This conclusion appears to be justified by a consideration of the solubilities of the different resins as prepared by us. The uncured and less mature resins are more soluble in any solvent. Since swelling may be considered essential to the gel dissolution process, we may reasonably expect that the capillary condensation as it proceeds is a process that separates and disperses the resin molecules. The degree of dissolution appears to be related to the steepness of the isotherms in the final stages of the sorption process.

A comparison of the isotherms for a series of resins at 35° and 50° for either vapor, and a consideration of the previous table of pore sizes lead us to conclude that the smaller capillary spaces of the less mature resins are capable of holding a larger quantity of liquid than are the sum total of small and large capillary active spaces of the more mature resins. For the latter resins it is possible to obtain much more accurate values for x/m as we approach the saturation value. Thus the matured resins have a greater tendency to retain some of their original structure that holds the mass firmly together, and complete dissolution by a capillary condensation process is impossible.

Reversibility of the Sorption Process. As sorbed liquid is withdrawn from an elastic gel, the gel molecules again approach each other to give a more closely packed structure. This behavior distinguishes swelling gels from nonswelling gels. If the vapor pressure of the sorbed liquid is decreased to a negligibly small value, all sorbed vapors are eventually removable, and the gel returns to its original structure and volume. This behavior of swelling gels has been typical of the gel systems previously studied, and is also undoubtedly typical of the gel system investigated in this research. On the whole the swelling gels could be classified as dried out gels, for they were originally deposited from a solution of some kind. It is quite natural to assume that such gels after swelling in a given liquid would return to their original structure and volume. In this research a gel of vitreous nature has been studied in its behavior as a swelling gel, with acetone and methyl alcohol vapors as sorbates. A complete desorption of vapors has not been effected in any case because of the time which would be required, but an inspection of the series of sorption and desorption isotherms and of the assumed equilibrium curves for more mature resins reveals that a considerable portion of the curve is reversible. Actually, and for practical purposes it may be said that the last traces of vapor, taken up in the region of low relative saturation pressures, are held so tenaciously that we could not, in any such experiment as performed here, expect to attain complete desorption. The blushing of varnishes has been attributed to such a retention of certain solvents which take on moisture from the atmosphere when the humidity is exceptionally high.

Rate of Sorption and Desorption. In studies of the sorption of water by wood Pidgeon and Maass[4] found that their final equilibrium was generally reached from the dry state in under half an hour in the case of moderate vapor pressures, while the corresponding desorption process required several hours. Polanyi and Welke[5] found that periods even up to 2 and 3 days were necessary for the attainment of equilibrium for the adsorption of gases on charcoals. In the case of the glyptal resins it was found that relatively long periods of time (at least 24 hours) were required for the sorption process and that even much greater periods were required for the desorption. Equilibrium was always most difficult of attainment in the region of low vapor pressures. There are given below two graphs (Figs. 5 and 6) which have been prepared to indicate the rapidity with which the sorption and desorption processes come to equilibrium.

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[4] J. Am. Chem. Soc., **52**, 1053 (1930).

[5] Z. physik. Chem., **132**, 371 (1928).

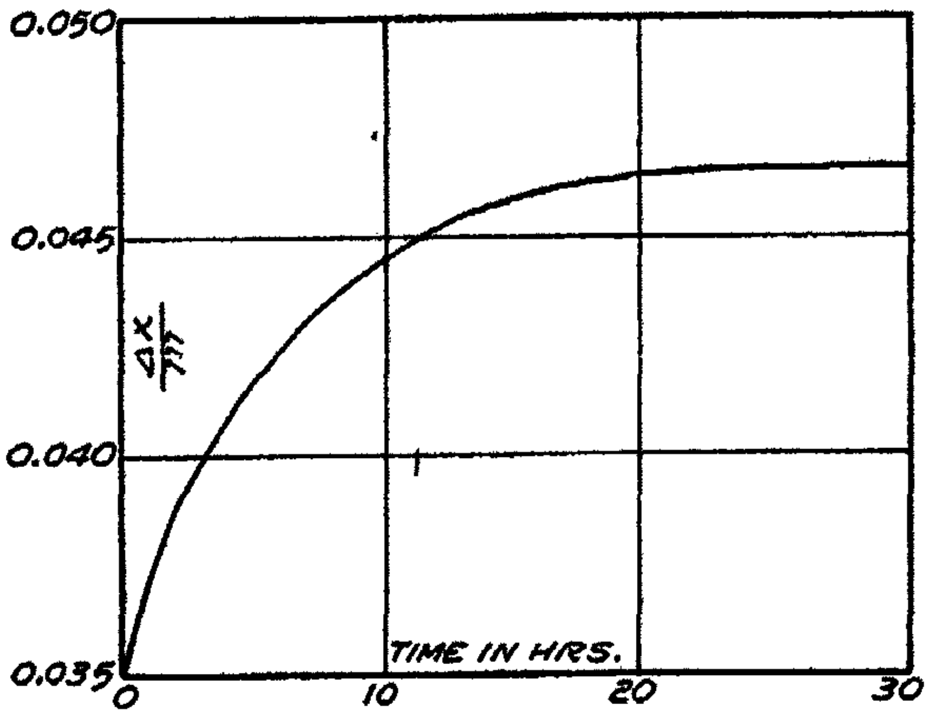

FIG. 5

Sorption—Time Curve
Acetone—50° Sorption on Cellulose Acetate
Change in p_x/p_s 0.109 to 0.230

It is believed that our data are sufficient to justify our method for determining the position of what we call the true sorption isotherms. The only real difficulty in coming to an equilibrium was found in the region of low relative pressures. In the condensation region the sorption and desorption curves were reasonably reversible. The positions of equilibrium could also be determined with some accuracy in the region of the transition from adsorption to condensation. The more mature resins always gave better reproducibility, probably due to a greater rigidity of structure and larger size of capillary.

Thus, any hysteresis which our data and curves indicate is to be found in the region of low relative saturation pressures, and is probably to be explained on the basis of a closely knit structure that is only slowly permeated by gases and vapors. It has been noted that the most mature resins with their greater rigidity of structure show the least hysteresis. In the hysteresis region it

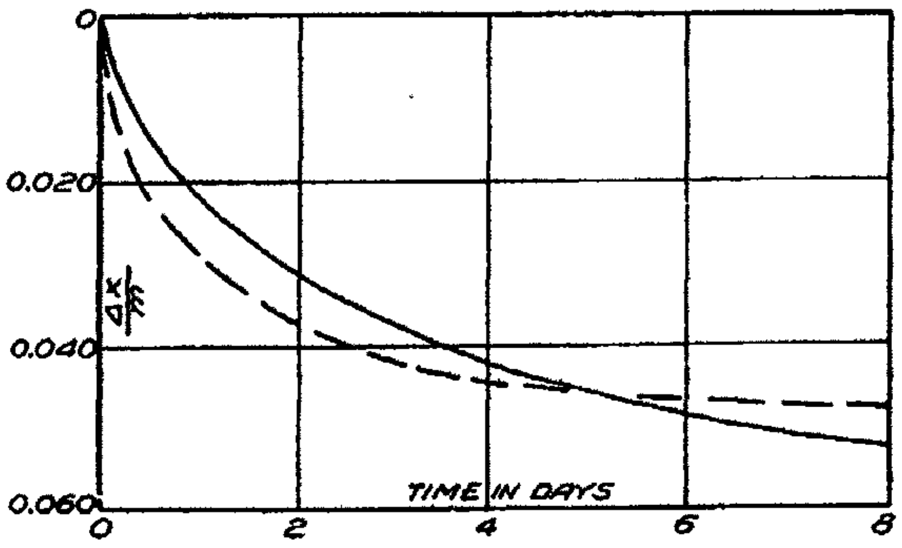

FIG. 6

Desorption—Time Curve
Acetone—50° Desorption
———— Resin I
— — — Resin III
Change in p_x/p_s 0.613 to 0.011

seems likely that associated structural units have become separated with the breaking of secondary valence bonds, and molecules of either acetone or methyl alcohol have been taken up due to this condition of unsaturation. Such a coupling would probably result in a permanent adsorption of the polar sorbate molecules and may be objected to on that account. Nevertheless we were never able to remove a considerable amount of the sorbed vapors from the resin samples in a closed desorption system in which the vapor pressure was never greater than 2 mm of mercury for a ten day period. Experiments were made with a cellulose acetate sample and a considerable hysteresis was was observed. However, there was never any difficulty in removing the methyl alcohol and acetone vapors at very low pressures.

It is also of interest to note that the resins took up the initial vapors of methyl alcohol more rapidly than those of acetone, although the materials are actually more soluble in the latter substance. This suggests that the smaller molecule was better able to penetrate the structure of the resin. However, our data must be considered insufficient to establish this as a general conclusion, since only two kinds of vapor were considered.

Molecular or Particle Weight. The experimental work of this article has made it possible to make several statements with regard to the structure of the glyptal type of resin. Of necessity these statements have been largely qualitative in nature. Perhaps the most important question to be answered is whether the fundamental structural units are giant molecules (sometimes called macromolecules) or micells. We have expressed our opinion in favor of the macromolecular structure because of the changes in the position and shape of the sorption isotherms for the several resins. The further conclusion has been drawn that the size of these giant molecules, particularly as regards their length and complexity, is increased as the time of the curing process is extended.

However, this research may be considered to be only the beginning of a number of studies which may be expected to lead to the construction of a model which will represent the physical and chemical behavior of the resin. The most immediate and important single task seems to be the determination of the molecular weight, because the properties of the material will certainly depend upon it. There are several methods available to us which should make this possible, the most promising of which are viscosity and dielectric constant studies of the resins in dilute solution. The theory by which the viscosities of the dilute solutions may be related to the molecular weights has recently been reviewed by Staudinger,[6] so that it will not be given here. The method which involves dielectric constant determinations is an application of the dipole theory of Debye. It depends upon the fact that owing to the frictional resistance of the medium to the rotation of suspended molecules or particles a finite time is required for their orientation in an alternating electrical field. If the frequency dependence of the dielectric constant is determined for such a system of electrically dissymetrical particles dissolved in a liquid medium there will be found to be a region in which the dielectric constant decreases as its

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[6] Z. physik. Chem., 153, 391 (1931).

frequency is increased. The theory, which has been discussed by Marinesco[7] and also later by Williams and Oncley,[8] expressed the size and therefore the weight of the dissolved macromolecule in terms of the observed critical frequency and the true inner friction constant of the medium. Both types of molecular weight study are now in progress in this laboratory.

Summary

1. An apparatus for the study of the sorption of vapors in a gas free atmosphere has been described. It makes use of a quartz balance of the McBain-Bakr type.

2. The sorption and desorption of acetone and methyl alcohol vapors by glyptal resins maintained at 35° and 50° have been systematically investigated.

3. It has been possible to draw a number of conclusions and make several calculations from these data, as follows:

a. Equilibrium isotherms characterize the resin as a typical swelling gel.

b. The model chosen to represent the glyptal resin, based upon the assumption of giant molecules as the fundamental structural units, is believed to be consistent with the experimental results.

c. The first part of the sorption curve is probably due to a surface adsorption, while the last part is due to the purely physical process of the condensation of the vapors in capillary spaces. The transition from one process to the other is indicated by an intermediate region.

d. For the cured glyptal resins there are indicated a more firmly knit structure and a larger molecular or particle size. These changes become more and more pronounced as the time of an arbitrary curing process is increased.

e. The free energy change as the sorption process at 35° and 50° continues has been calculated.

f. From the free energy changes and their temperature coefficients the differential heats of the sorption process have been calculated. These data indicate that the last sorption process is one of simple condensation of the vapors in the capillary spaces.

g. Calculations have been made for the size of the interconnecting capillaries in the partially swollen gel. These capillaries have been formed by the filming of the structural units in the first stages of the sorption process.

h. The tendency for a resin to become completely dispersed in a solvent is shown to decrease as the time of the curing process is increased.

i. The ability of the resins to retain considerable amounts of adsorbed vapor is commented upon.

j. It seems probable that except for the very low pressure regions any hysteresis observed is apparent rather than real. This is indicated not only by the experimental data but also by thermodynamical considerations.

4. Corresponding data were obtained for a sample of cellulose acetate and its behavior was compared with that of the several glyptal resins.

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[7] J. Chim. phys., 28, 51 (1931); Kolloid-Z., 58, 285 (1932).

[8] J. Rheology, 3, 271 (1931).

FILTRATION PHENOMENA IN COLLOIDS

BY MAY ANNETTS

Colloidal solutions are usually assumed to be unaffected by filtering. But in some cases it has been found that filtering produces important changes—it is the purpose of this paper to outline and explain these changes.

In the course of some recent experiments the following curious effects were observed with Arsenious Sulphide Sol.

(1) The conductivity decreases, sometimes as much as 50%, when it is passed through a filter paper. One would expect that, if the conductivity changed at all, it would increase, due to the addition of electrolytic impurities from the filter paper.

(2) When the colloid is repeatedly passed through the same piece of filter paper its conductivity decreases to a constant value—Graph I.

(3) Repeated filterings of the colloid, each time through a fresh piece of filter paper, cause the conductivity to decrease to a minimum and then increase. These results are shown in Graph II.

(4) The conductivity of a sol which has been filtered, one or many times, increases when it is allowed to stand for some time after filtering—Table I.

TABLE I

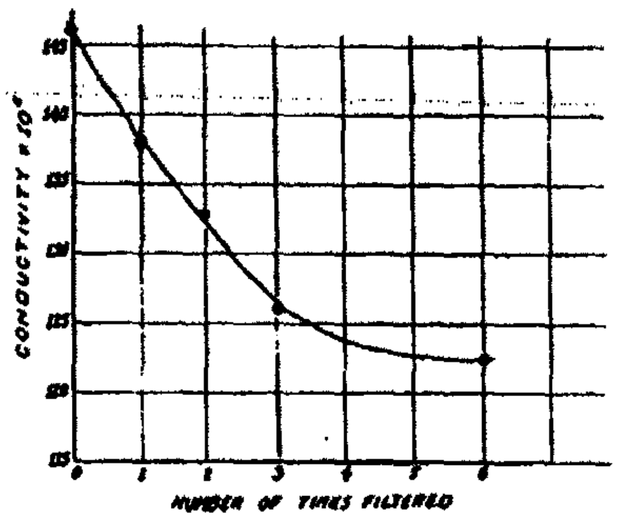
No. of times filtered	Conductivity $\times 10^6$	
	11 A.M.	4 P.M.
0	167	167
1	77.5	92.0
2	49.5	58.0
3	47.7	55.8
4	55.5	57.7

(5) Sols which have been filtered many times coagulate on standing; in fact, if filtering is continued long enough, the sols will filter only very slowly and finally coagulate as they filter.

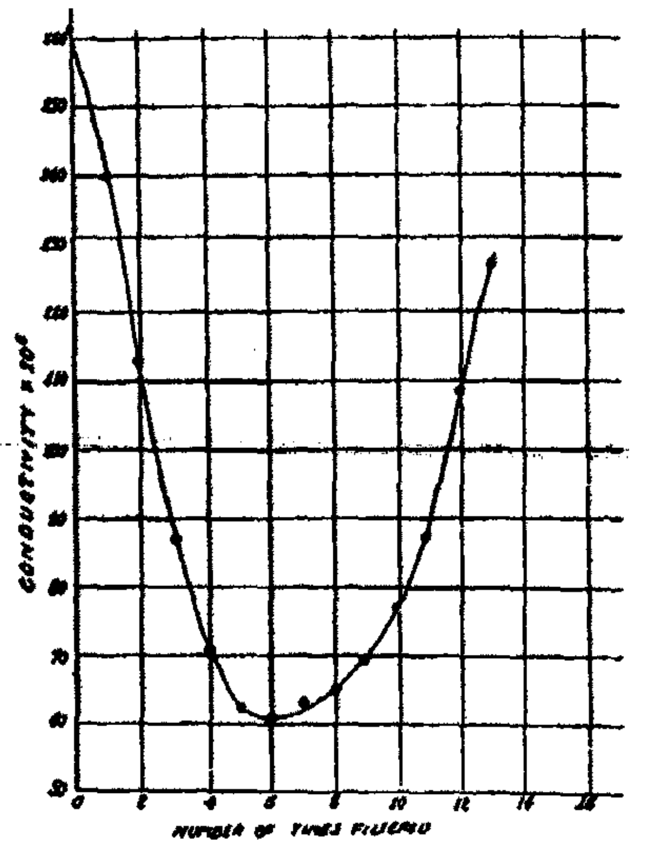
(6) That the effect is dependent on the amount of sol filtered is shown in Graphs III and IV. In Graph III various amounts of sol are filtered, each through a separate piece of filter paper; in Graph IV 25 cc samples are successively filtered through the same piece of paper, the filtrates being kept separate.

(7) The effects are larger when low grade filter paper is used than when especially prepared ashless paper is used, further the effects are reduced by successive washings of poor filter paper with distilled water. The results listed above were obtained using Whatman's No. 1 paper washed with distilled water.

In an attempt to isolate the material causing the initial decrease in conductivity, series of readings were taken using various components of the sol. Each series consisted of conductivity measurements after successive filterings, using a fresh piece of filter paper for each filtering. The results for distilled water, Arsenious Oxide, and Hydrogen Sulphide are shown, from right to left, in Graph V. None of these curves shows the initial decrease which characterizes Graph II. It was therefore thought that the effects might be in some way connected with the colloidal state, so measurements were taken of the conductivity before and after once filtering various sols. Results are shown in Table II. It will be noticed that a decrease occurred only in the two cases where we have both free hydrogen ions and rather high conductivity. Since filter paper has a negative charge it might be expected to adsorb hydrogen ions—which would decrease the conductivity. Measurements of pH were therefore made using a quinhydrone electrode with a calomel half cell and potentiometer. The pH was found to increase linearly with the number of times filtered, whatever the material used, and irrespective of whether the conductivity was increasing or decreasing—see Graph VI.



GRAPH I

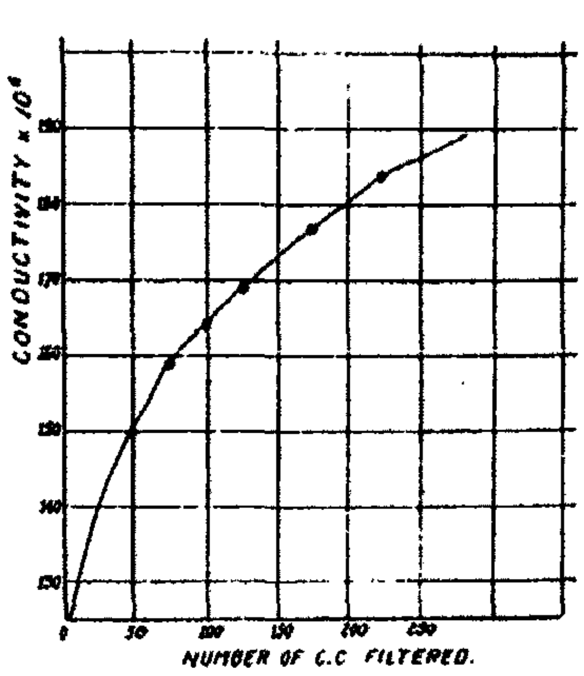


GRAPH II

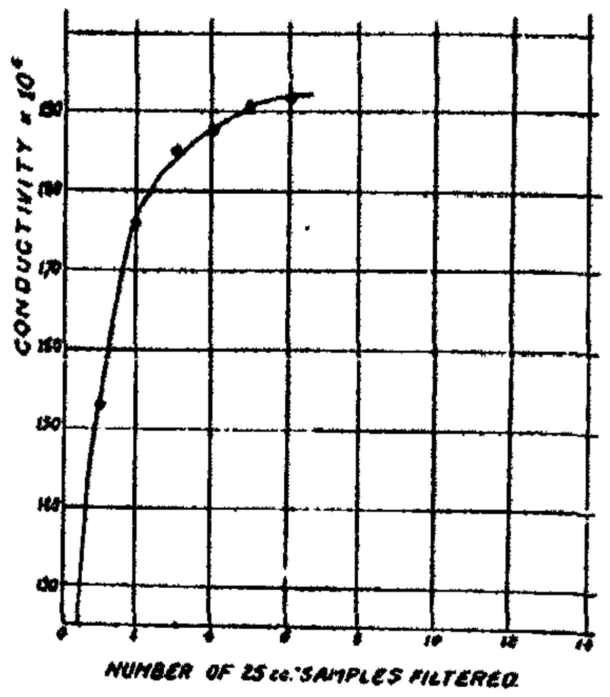
TABLE II

Name of sol	Conductivity × 10^6 Before Filtering	Conductivity × 10^6 After Filtering
Copper	24.6	60.2
Gold (Zsig.)	1400	1400
Gum Mastic	18.3	41.5
Prussian Blue	58.2	88.2
Ferric Hydroxide	3540	3330
Green Gold (Catechol)	864	725

This suggests that the observed results on filtering may be explained as due to the combination of two effects, (a) an increase in conductivity of the sol due to the addition of electrolytic impurities dissolved from the filter paper,



GRAPH III

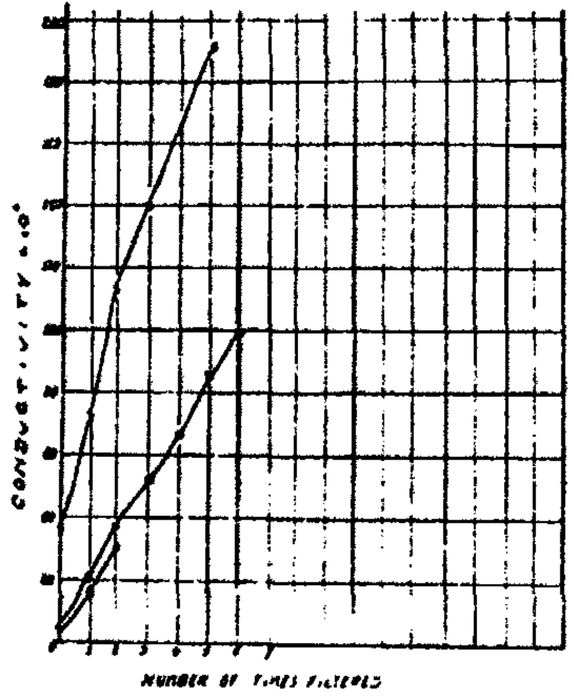


GRAPH IV

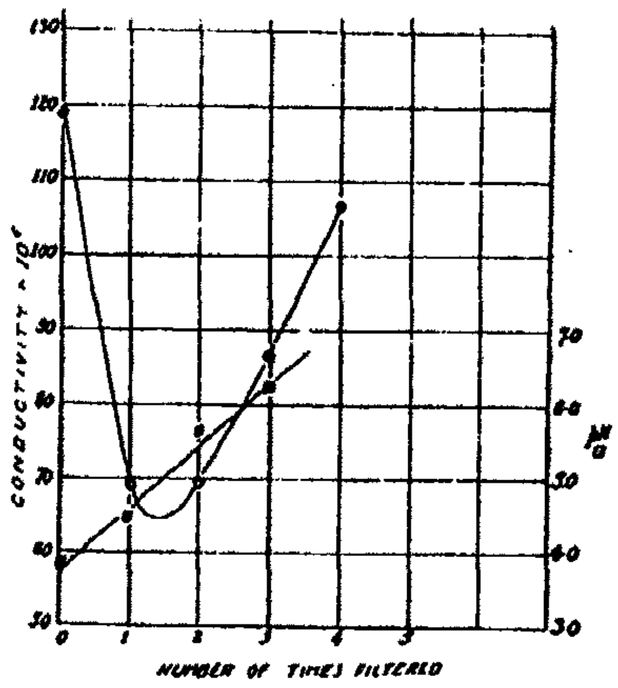
(b) a decrease in conductivity of the sol due to the adsorption of hydrogen ions by the filter paper. Effect (a) will be large when the initial conductivity is small, i.e., when the total number of ions already present is small. Thus when the number of free hydrogen ions is large and the conductivity is large, effect (b) will be large and effect (a) small, so that the resultant effect will be a decrease in conductivity; whereas, when the number of free hydrogen ions is small and the conductivity small effect (b) will be small and effect (a) large, so that the resultant effect will be an increase in conductivity.

If the above reasoning is correct, a dilute solution of hydrochloric acid might be expected to show a decrease in conductivity on filtering, and a sodium chloride solution of the same strength an increase in conductivity. Experiment verifies these predictions. The curve for conductivity of hydrochloric acid with successive filterings is shown in Graph VI.

If the amount of electrolytic material in the filter paper is small, these hypotheses explain why the effect is dependent on the amount of sol filtered,



GRAPH V



GRAPH VI

and why a constant value of the conductivity is obtained by filtering repeatedly through the same piece of paper. Further, it is consistent with the above that the effects are larger with low grade paper than with especially prepared ashless paper; though to explain the larger decrease in conductivity with the poorer paper we must assume that the impurities are responsible for part of the adsorption of ions.

The behaviour of hydrogen sulphide solution may also be accounted for on this theory. It is very weakly dissociated and hence has few free hydrogen ions, while its conductivity was quite low (about 1/5 that of arsenious sulphide sol) for it was prepared from distilled water.

An arsenious sulphide sol is stabilized by hydrogen sulphide adsorbed around the particles. Thus when few hydrogen ions are removed from the intermicellar fluid equilibrium is destroyed and part of the hydrogen sulphide from the double layer released as free ions. This explains the increase in conductivity and pH on standing, also the decrease in stability of the colloid with successive filterings.

Let us consider a sample of arsenious sulphide sol. Before filtering its pH was 4.05 and its resistance 3800 ohms at 25°C, in a cell whose constant is 0.33. After filtering once its pH became 5.35 and its resistance 6900 ohms at 25°C.

Before filtering, no. of hydrogen ions per cc $= 6.2 \times 10^{23} \times 10^{-3} \times .89 \times 10^{-4} = 5.5 \times 10^{16}$. After filtering no. of H^+ ions per cc $= 6.2 \times 10^{23} \times 10^{-3} \times .45 \times 10^{-5} = 2.8 \times 10^{15}$. No. of H^+ ions lost $= 5.2 \times 10^{16}$. The effective current produced by these is $(5.2 \times 10^{16})\ (1.59 \times 10^{-19})(.00349) = 2.9 \times 10^{-6}$ amps. The original conductivity of the sol $= .33/3800 = 8.7 \times 10^{-5}$ reciprocal ohms per cm^3. After filtering once conductivity of the sol is $.33/6900 = 4.8 \times 10^{-5}\ cm^3$. Therefore loss in conductivity is 3.9×10^{-5}. Loss caused by the removal of hydrogen ions is 2.9×10^{-5}. So that the filter paper must adsorb some ions other than the hydrogen, as one would expect.

The linear relation between pH and number of times filtered means that the number of hydrogen ions adsorbed, y, is proportional to the number of hydrogen ions present, C *i.e.* $y = aC$ where a is a constant. The average of several sets of readings gives $a = 0.9$ which means that practically all the free hydrogen ions are adsorbed in the first few filterings.

From the resistance changes after many filterings we can calulate the equation representing the addition of electrolyte from the filter paper to the sol. It is found that the change of resistance on filtering, y, is proportional to the square of the resistance before filtering, R *i.e.*, $y = b R^2$. Since this equation holds for all but the first few filterings, the adsorption of ions other than hydrogen must take place during the same time as the addition of hydrogen ions.

Thus changes in conductivity, pH, and stability may be expected to accompany the filtering of suspensoid sols.

In conclusion, the author wishes to express her sincere appreciation to Prof. E. F. Burton of the Department of Physics at the University of Toronto, for his helpful suggestions and advice throughout the investigation.

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REVIEW OF RESEARCH ON CANE WAX IN RAW AND REFINED SUGARS

BY C. F. BARDORF AND J. A. B. BALL

Introduction

The object of this paper is to bring under review a few of the practical aspects of colloidal phenomena in the sugar industry and more specifically those due to Cane Wax.

The complex nature of the juices from the sugar cane and the sugar beet soon obtruded itself upon the attention of the pioneers of the industry, and there is no doubt that the now universally practiced diffusion of beet chips (cossettes) was largely influenced by Graham's classic studies. In the case of beet root tissues the application was obvious. Each tiny cell in the root can be regarded as a dialysing sack, and as such can hold back a large proportion of the colloids and allow the crystalloids to pass into the diffusion water.

In connection with cane juice, however, diffusion processes appear to offer insuperable difficulties. Grinding and milling of the cane is therefore the almost exclusive practice by which a high yield of sugar can be obtained from the cane.

But by this method a large percentage of the colloidal substances are forced into the juice and can be only partially removed by processes more or less based on a common principle.

Non-Sucrose Substances in Cane Juice

As the major part of the work on sugar juice colloids has been directed to those in sugar cane juice, it may be well to give these exclusive attention. But it may be mentioned, in passing, that some thirty years ago the senior author incidentally isolated a quantity of beet sugar wax, which, unfortunately, received only casual attention at the time. This wax, though chemically different from cane wax, had similar physical properties. It contained much nitrogen; on dry distillation it yielded an oil of pyridine-like odor and from an alcohol extraction a wax was obtained quite similar to the alcohol soluble portion from cane wax.

The juice expressed from the cane by the ponderous rollers of modern cane mills is a muddy, olive green or brownish liquid, laden with solid particles ranging in size from macroscropic masses to the ultramicroscopically divided emulsoids—the cane wax complex which has of recent years employed the attention of industralists and chemists.

In the "mixed" juice, *i.e.*, the united juices from all the sugar mills in tandem, many substances may be found which contribute to the colloidal phenomena in sugar solutions. Some of these substances can be removed easily, while others pass through, in an exceedingly small amount, into the best products of the refiner's art.

Listing the suspensoid particles roughly in the decreasing order of their size, we have bagacillia (small pieces of cane tissue) fine sand, clay, insoluble organic salts of calcium, and then the true dispersoids, such as colloidal silica, and other non-dialysable substances; proteids and pentosans, pectin, etc., and lastly gums and waxes which assume suspensoid and emulsoid forms when the juices are heated or when the defecated juice is concentrated. Concentrated, defecated juice, generally known as "syrup" is the "meladura" of Latin America.

Because of the persistant migration of the cane wax complex through all the processes of sugar making,[1] it may be inferred that it is present in a very minute state of dispersion. Cane wax is undoubtedly the most troublesome of all impurities which has to be dealt with by the defecation methods applicable on an industrial scale, because it adheres so tenaciously to all solids it may contact.

Colloids in Mixed Cane Sugar Juice

Confining ourselves for the moment to the consideration of mixed cane sugar juice we have an impure, thin (15% solids) sugar solution copiously laden with suspended particles. Under defecation methods, common in principle but varied in detail to accord with the nature of the juice, milling practice, etc., the coarser, mechanically introduced particles are, to a large extent, easily separated. Next in order may be considered those substances which are acted upon by heat and chemical reagents. Sulphur dioxide gas being employed for specific purposes only, milk of lime may be said to be the exclusive agent used in practice, and is made to react with the impurities of the juice at a temperature of 100°C or over.

From the so-treated juice, vegetable proteids are coagulated and some organic and inorganic salts precipitated. The flocculent precipitates thus formed trap most of the larger suspensoids and some of the cane wax in the form of emulsoids. These then pass out of the system in the defecation mud. But even with the most carefully controlled pH regulation and the exercise of other precautions, some colloids remain in the defecated juice and require subsequent attention. These highly dispersed substances adhere to and are occluded by the sugar crystals during the process of boiling to grain, be it from raw or refined liquors. When, therefore, raw sugar crystals are dissolved in the refinery the emulsoid colloids in particular, pass through all the stations of the refinery, and some are easily detectable in all granulated sugar. If these raw and refined sugars be specially treated, a variety of unremoved substances can be separated. But one of the difficulties is the question of what procedure shall be followed in the endeavour to separate all suspensoids in order that some reliable quantitative as well as qualitative data may be recorded. Quantitatively it is primarily desirable to determine the total amount of colloids, of all forms, residual in the finished products. The great difficulty in this direction is to free the separated colloids from the last traces of sugar without washing away some of the colloids themselves, which,

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[1] Bardorf: Ind. Eng. Chem., 20, 258 (1928).

despite their troublesome nature, are present only in very minute quantities. Qualitative examination has its difficulties because of the complex nature of the colloids, and their tendency to physical change when subjected to ultrafiltration or dialysis. Coagulation takes place so that one colloid traps and occludes another and a pure chemical product is not obtained.

Four Classes of Colloids in Raw and Refined Sugars

From the now large number of investigations on the non-dialysable matter in sugar solutions, syrups and molasses, a fourfold, broad classification has been made by the authors, a classification chiefly based on the physical properties of the complex, *viz.*, (1) Acetone soluble, soft wax; M.P. 52°C; (2) Alcohol soluble brittle wax, M.P. 82°C; (3) Water soluble, not fusible; (4) Insoluble, not fusible, contains nitrogen compounds.

This classification of raw sugar colloids is prompted by the data established by the authors from the dialysis of three typical raw sugars. It was found that the three types, although containing approximately the same percentage of sugar (96%) varied greatly in respect to quality and quantity of non-dialysible matter. Uniform solutions of the three sugars were prepared for dialysis through collodion sacks[3] and the colloidal matter collected, dried and weighed. The percentage of non-dialysable material so found ranged from 0.15% to 0.38%, but the diversity in its composition was more marked than the relative quantity present. This remarkable diversity was brought sharply to notice upon submitting the complex mass to fractional extraction, using acetone, alcohol and water as the solvents, in the order named.

In the case of the three sugars under examination we obtained the following results:

TABLE I

Non-dialysable Material from Raw Sugars

Source of sugar	% Non-dialysable material
*B. W. I.	0.24
Cuban	0.25
San Domingo I	0.15
†San Domingo II	0.38

* B.W.I.—British West Indies.
† A poor grade of sugar.

The distinctive character of the extracts, as classified in preceding paragraphs, is apparent in this, that if the acetone and alcohol extracts only be taken as denoting the true wax-like material, the B. W. I. sugar contains 0.057%, the San Domingo I, 0.185%, and the Cuban 0.153%, since the fractional extraction of the undialysable portions obtained showed them to consist of the following fractions:

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[3] Cf. Holmes: "Laboratory Manual of Colloid Chemistry," 23 (1928).

TABLE II

Fractional Extracts from Non-dialysable Material

Solvent	San. Dom. I.	B.W.I.	Cuban
Acetone	14.95%	13.14%	27.20%
Alcohol	33.68%	10.80%	34.29%
Water	26.73%	58.50%	not determined.
Insoluble	24.64%	17.55%	

A further divergence in the composition of the acetone, alcohol and water soluble portions of the colloids is shown in the ash contents of the extracts, as illustrated in Table III.

TABLE III

Ash Content of Wax Complex

Extract	San Domingo % Ash	B.W.I. % Ash
Acetone	0.63	1.55
Alcohol	3.64	19.07
Water	29.87	18.00

Adsorption of Wax Complex

(by Comminuted Materials)

After a series of investigations the authors have come to the conclusion that of the many constituents of non-dialysable substances present in raw sugars, there are two, at least, which resist all heretofore practiced technical procedures for their complete elimination from refined sugars, even from those of the highest purity. There are several phenomena which seem to substantiate this opinion, although it is a fact that the acetone and alcohol soluble constituents of the cane wax complex are tenaciously retained by such materials as filter cloth, diatomite, paper pulp and bone black. We have been able to extract appreciable quantities of the wax constituents from the first three mentioned materials. This property of the complex is of significance, since no amount of washing with hot water (90°C) will remove any appreciable amount of it. This is illustrated in Table IV.

TABLE IV

Wax Complex retained by Filter Cloth, Diatomite and Paper Pulp

	Cloth	Diatomite	Paper Pulp
Acetone soluble	0.95%	1.79%	2.74%
Alcohol soluble	0.41%	1.79%	0.94%
Total	1.36%	3.58%	3.68%

A noticeable feature in this table is that although the melting point of the acetone soluble is 52°C, and the alcohol soluble is 82°C, the wax of the lower melting point is more persistently held by the cloth tissue and paper pulp than its alcohol analogue.

In regard to bone black adsorption of the complex, Paine and Badollet[3] have investigated the adsorption of what they call reversible and irreversible colloids, and find that bone black exhibits a preferential adsorption for reversible colloids, which, it appears, is dependent on the quality of the bone black —the more active blacks have a decided preference for the reversible form. In this connection the authors would refer to their paper on "Filtrability and Refinability of Raw Sugars"[4] in which it was pointed out that in their experience with raw sugars from the Uba cane, "the bone char rapidly reached a stage of saturation with respect to colloidal matter, which it then appeared to give up indiscriminately to water or any brilliant syrup . . . heat tends to coagulate the colloids in such syrups."

Paine and Badollet admit that their distinction "reversible" and "irreversible" is more or less arbitrary. They say: "For instance if the period of heating of the dried residue (of colloids) is extended the proportion of water-irreversible colloids is increased, a portion of the reversible colloids becoming irreversible (presumably by hydration)."

In this connection Dr. Steacie, in a lecture at the McGill University, contended that colloidal particles of the same composition assume various physical characteristics dependent upon the numerical conjunction of their molecules. In the light of this statement it would appear that "reversible colloids which may become irreversible" or "emulsoids and suspensoids" merely become terms used to distinguish the varying physical properties of the same colloid.

The numerous "amorphous" activated carbons on the market exhibit properties similar to bone black in the adsorption of colloids, and it is largely to this that they owe their value as auxiliary refining agents.

We can now pass on to an important question, *viz.:* What is the nature of the colloids found in refined sugar products, from the purest white crystals (granulated sugar) to soft sugars of all grades (yellow or brown)?

In so far as no determinations have been made on the distinctive characteristics of acetone and alcohol soluble components of cane wax, we do not know which of the two is the more resistant against complete elimination from the refined sugar product. There are, however, at least two considerations which would lead us to feel convinced that it is the acetone soluble which is present in greater percentages in refined sugars.

In our previous paper[5] on the subject, we designated the acetone soluble by the letter "*G*", and the alcohol soluble by "*B*." These terms were chosen for brevity's sake, *G* being assigned to the acetone soluble because this fraction was usually of a greenish colour, while the alcohol soluble was brown.

If we now calculate the percentage of the *G* in the G-B wax extract $100G/(G-B) = \%G$, we obtain certain percentages of *G* which are quite significant. A study of these percentages would seem to indicate that in those sugar solutions, and the sugars obtained from them, which have received

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[3] Planter Sugar Mfr., **79**, 21 (1927).

[4] Intern. Sugar J., **29**, 375 (1927).

[5] Bardorf: Ind. Eng. Chem., **21**, 366 (1929).

the least treatment or purification, the G fraction is present in the neighborhood of 50%, while in similar solutions and sugars therefrom, which have gone through refining processes, the G content is over 50%.

Analysis of the data given in Table V, tends to substantiate this contention.

TABLE V

Percent "G" in Raw Sugars and Solutions

Normal raw sugar	51%
Crusher juice	50%
First Mill juice	51%
Second Mill juice	65%
Defecated juice	40 to 60%
Average in Cuban Raw Sugars, three seasons	52%
Cuban Raw, 1926	49%
Cuban Raw, 1928	63%
B. W. I. Raws, 1926	39%
Final Molasses	52%

Percent "G" in materials in contact with sugar solutions during refining

Filter cloth	70%
Diatomite	50%
Paper pulp washed @ 88°C	74%
Paper pulp washed @ 65°C	64%
Refined sugars from the vacuum pan	72%

A few words of comment may be necessary to explain two or three apparent anomalies in this table. The remarkable rise of *G* wax in the second mill juice is due to the addition of water, known as (maceration or inbibition water) to the bagasse, thus augmenting the emulsifying action of the rollers. The *G* percentage is nearly always highest in juice from the second roller set, as it is here that the most of the colloids are forced into the juice. From actual determinations of *G* in juices flowing from a four tandem mill the percentages were respectively 47, 67, 55 and 65. The crusher juice was 46%.

The high percentage of *G* in Cuban raw sugars of 1928 is consequent upon the large proportion of old and burned cane ground at the mill from which the sugar was sampled. That only 50% of *G* was found in the diatomite lies in the fact that the filter aid was used exclusively, in this case, for the pressing of liquor from washed raw sugar crystals, and must therefore contain the same relative percentage of *G* as the raw sugar itself.

Minute Presence of Colloids in Granulated Sugar

There are several further facts to substantiate the conclusions drawn from the acetone soluble percentage of wax extracts in raw sugar products as compared with the percentage in refined products.

A standard grade of granulated sugar may certainly be regarded as one of the purest of food products, being comparatively chemically pure. For instance, ten samples of such sugars were found to contain ash ranging from a minimum of 0.002% to a maximum of 0.016%, having an average of only 0.008%.

While the presence of colloidal matter may almost always be observed, the quantity present must be exceedingly small. The authors know of no direct reliable method for the quantitative determination of colloids in granulated sugar, but there are several by which it may be inferred that the colloidal content is 10 per million parts of sugar, or even less. To determine this emulsions were made quantitatively of extracted fractions of acetone, alcohol and water soluble colloids, and their opacities and colouring qualities studied.

Acetone Soluble Wax the Predominant Colloid in Granulated Sugar

To three separate volumes of a 50% solution of water-white granulated sugar were added the three fractions of colloids respectively, in the proportion of 10 parts in 1,000,000, brought up to 100°C and well shaken. Examination by the Lovibond tintometer showed that the acetone soluble fraction imparted one unit of colour, the alcohol soluble sixteen units, and the water soluble eighty units. But the tint imparted to the solution by this quantity of the water soluble fraction was far greater than would ever be met with in any granulated sugar of reasonably good quality. On the other hand the acetone soluble wax produces a more pronounced "colloidal haze" than does the alcohol soluble, and the water soluble the least of all. This phenomenon is more definitely displayed by comparing the relative strengths of Tyndall cone produced in the solutions under examination.

Closely related to this question, Badollet is developing a particularly interesting apparatus for the ultra-microscopic photography of colloids. He has applied this apparatus, in its present stage of development, to the examination of granulated sugar solutions, and has produced a large number of photographs in the study of this problem. Here again we have a confirmation of the occlusion of colloids by the growing crystals, even when the sugar liquors are of high purity and brilliant appearance when viewed by transmitted light.

We have a remarkable illustration of how the colloids are more or less occluded in proportion to the quantity present in the liquor charge from which the crystals are grown. A liquor of lower sugar purity, but relatively free of colloids will give a sugar exhibiting a feebler Tyndall cone than one boiled from a liquor of higher purity but more charged with colloidal particles. (Exhibit photographs):

"B" from high liquors.
"S" from colloid free syrup.
"O" from white liquor, but containing colloids.
Remelt.

Lastly, if a granulated sugar of large grain be washed with cold water so that in three consecutive washings each will contain about one-third of the sugar, the solution representing the outer layer of the crystal will invariably show the strongest Tyndall cone, while the third washing, representing the core of the crystal, will show the dimmest cone. From these and other considerations the authors conclude that of the four classes of non-dialysable material in raw sugars, the insoluble fraction is completely removed in the preliminary steps of the refining operations, *i.e.*, defecation and filter pressing. Of the other three the water soluble is absorbed up to 90 or 95% by bone black, but the acetone and alcohol soluble colloids migrate through all the stations of the refinery, and their presence is detectable in all granulated and soft sugars.

From these data we may hope that by the refined optical methods, now being developed, some definite quantitative and qualitative information will eventually be obtained. Closely related to Badollet's photographic work is that of Balch[6] with the Spectrophotometer and Zerban and Sattler[7] with the recently introduced Pulphrich photometer. Zerban and Balch have evolved mathematical formulae from which both investigators have been enabled to construct instructive tables on Tyndall cone intensities. Zerban has shown that in this respect certain anomalies have still to be investigated before the light phenomena can be thoroughly understood.

For a fairly complete bibliography of the large number of articles on Cane Juice Colloids, Farnell's[8] report may be consulted. In this report the chemical as well as the physical properties of the colloids are discussed in many important details; thirty-three references are given.

Much of the work above alluded to had to be carried out on sugar Centrals themselves, and the authors wish in particular to thank the Eastern Cuban Sugar Corporation, and the American Sugar Refining Company for the cooperation and hospitality of their Cuban estates, and Dr. Schlegel of the National Sugar Refineries, for his help in collecting, washing, and sending samples of paper pulp used for the filtration of raw sugars.

St. Lawrence Sugar Refineries,
Montreal, Canada.

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[6] Ind. Eng. Chem., Anal. Ed., 3, 124 (1931).

[7] Ind. Eng. Chem., Anal. Ed., 3, 326 (1931).

[8] Intern. Sugar J., 26, 420 (1924).

ON THE NATURE OF COAGULATION VISCOSITY, AND THIXOTROPY IN COLLOIDAL SYSTEMS

BY S. S. KISTLER

Introduction

The most prominent division of colloids into classes is that into lyophilic and lyophobic. Many phenomena have been more or less satisfactorily explained on the basis of the differences in the relationship of the colloidal particle to the dispersion medium in these two groups. It has been assumed with considerable justification that the lyophilic particle is closely associated with a comparatively large quantity of the dispersion medium, and numerous investigations have had as their goal the measurement of the amount of "bound"[1] solvent. Although the results unquestionably lead to the conclusion that there are large differences in this relationship of dispersed to dispersing medium, quantitatively there has been little agreement between the various methods used.

The conception of "bound" solvent has led to the general conclusion that a certain amount of the solvent is held in more or less of a rigid condition within or surrounding the micelle. The author[1] has shown quite conclusively, however, that at least in the case of certain of the hydrated sols and gels, the amount of water that can be held in anything like a rigid condition must be very small. The fluidity of the water in these cases investigated was found to be not widely different from that of pure water. Also, Briggs[2] in a recent very illuminating article has clearly pointed out that "bound" water in its usually accepted meaning is purely a fiction.

In spite of these objections, nevertheless, qualitatively there is no question of the large differences between the lyophilic and lyophobic colloids and the concept of solvation will undoubtedly continue to be useful although its exact meaning remains unknown.

The Existence of Cybotactic Complexes in Liquids. In recent years considerable progress has been made in our understanding of the structure of liquids, and I feel that the time has come when these findings can be applied to our knowledge of colloidal systems with much clarification of mooted subjects. X-ray investigations[3] apparently indicate conclusively that within liquids the molecules are constantly associating into evanescent complexes of crystal-like arrangement. Even in the case of liquid mercury Debye[4] has demonstrated the existence of these complexes. That these complexes must

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[1] Kistler: J. Phys. Chem., 35, 815 (1931).

[2] J. Phys. Chem., 36, 367 (1932).

[3] Stewart and Morrow: Phys. Rev., 30, 232 (1927); Stewart: Rev. Modern Phys., 2, 116-22 (1930).

[4] Debye and Menke: Physik. Z., 31, 797 (1930).

be widely different from true crystal nuclei seems certain from the fact that, although Stewart estimates that at any one instant a large fraction of the molecules in a liquid are thus associated, numerous liquids may be undercooled for long periods of time without crystallization. Richards and Harris[5] conclude from their observations on the scattering of light that in undercooled liquids there are evanescent amorphous complexes. Whether these amorphous complexes of Richards and Harris are the same as the crystal-like complexes of Stewart, Debye, and others, it is impossible to decide. It may be that they are the same but only upon undercooling of the liquid do the densities of the liquid and complex differ enough to scatter light appreciably. Stewart has applied the term cybotactic complexes to those that show evidence of crystal-like structure with X-rays. His definition is sufficiently broad and vague, however, so that for lack of a better term, I shall refer to all associations of molecules into transitory groups as cybotactic complexes and for convenience shall refer to them as cybomas.

Whatever the nature of the cybomas, their existence can scarcely be questioned. Within a liquid the molecules must be constantly associating into cybomas, remaining thus associated for a brief moment and dissociating again only to reassociate with other neighbors. How rigid these associations may be remains at present unknown, but it seems very reasonable to assume that for the brief period of its existence, a cyboma will behave as a single particle and go through Brownian movements. In fact, it seems a perfectly reasonable assumption that any one complex may not disappear in entirety but rather that it is experiencing growth and decay at the same instant. In other words, the probability for the existence of any small group of molecules within the larger complex in a rigid framework is independent of the probability for the complex as a whole, so that while new molecules are adding to the surface of the complex, older portions are at the same time liquefying. A single cyboma, therefore, may progress through the liquid by growth on one side and decay on the other. It may branch and the branches quickly split off or it may liquefy as a whole.

If there is some sort of orientation of the molecules within the complex, growth by orientation of liquid molecules at the surface may be more probable than the sudden association of a group of neighboring molecules into a coherent mass. Regardless of how these cybomas arise, it is to be expected that they will on the average consist of relatively few molecules and, therefore, will diffuse rapidly compared to the velocity of a moderate sized colloidal micelle.

Influence of the Surface of a Colloidal Particle on Cyboma Formation

If we consider an imaginary boundary in the undisturbed liquid, an equal number of cybomas will cross from each side in unit time due to Brownian motion. Suppose, however, that this boundary is replaced by the surface of a colloidal particle; there will now come to the surface in unit time the same number of cybomas as would have crossed the imaginary boundary. But the

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[5] J. Am. Chem. Soc., 54, 3799 (1932).

surface may materially influence the number that progress outward from it. In other words, the substitution of a solid surface for the imaginary boundary may materially affect the equilibrium conditions at this boundary.

Three possibilities exist: (1) The cybomas coming to the surface are reflected from it so that the same number will be leaving as approaching, or in other words, the equilibrium will be undisturbed. (2) The cybomas in contact with the surface disappear more rapidly on the average than those in the center of the liquid. Under these circumstances there will be fewer cybomas leaving the surface than approaching it, and when an equilibrium is established the concentration of the cybomas in the neighborhood of the colloïdal particle will be less than in the center of the liquid. (3) At the surface of the particles, the probability that neighboring liquid molecules will associate into a more or less rigid framework will be greater than the average for the liquid. In other words, more cybomas will leave the surface than will approach it, and when the steady state is reached there will be a concentration gradient established diminishing with distance from the particle. The second and third possibilities are represented by a and b respectively of Fig. 1. It seems probable that deviations from case (1) will be greater with (3) than with (2) since the concentration gradient built up in (2) depends on the number of cybomas in contact with the particle surface, whereas in case (3) it is independent of the number of cybomas present and depends only on the interrelationship between the surface and the liquid molecules.

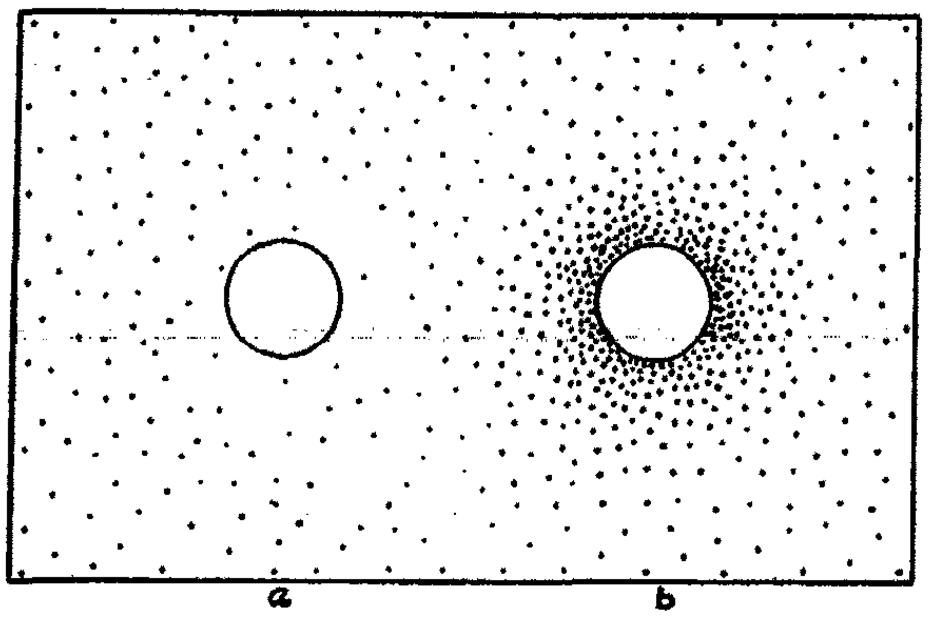

FIG. 1

Schematic arrangement of cybotactic complexes around a lyophobe and a lyophile particle

The number of cybomas in contact with unit area of a surface at any one instant must be small compared to the number of liquid molecules in contact at the same instant.

If we assume that there are *a* cybomas per second formed per unit volume and that there are kn_o cybomas vanishing, where n_o is the number present per unit volume, in the steady state

$$a = kn_o \qquad \text{or} \qquad n_o = a/k,$$

Assuming case (3), that is, a concentration of cybomas at the surface greater than n_0, and considering the surface to be plane it can be shown[6] that

$$n' = P'e^{-\sqrt{k/D}\,x}$$

where D is the diffusion coefficient, n' is the difference between the concentration at the distance x from the surface and n_0, and $P' = n'$ when $x = 0$. The expression for variation in concentration with distance fron the surface of a sphere is[7]

$$n' = \frac{r_0}{r} P'e^{-\sqrt{k/D}\,(r-r_0)}$$

where r_0 is the radius of the sphere.

Since we are totally in the dark as to the average size and average life of these cybomas, the best we can do is to make some reasonable assumptions and see where they lead us. Assuming that the average cyboma in water contains 10 molecules, that its density is the same as water and that its average life is 10^{-6} seconds, the curves of Fig. 2 were obtained for variation in n' with distance from a flat surface, a spherical particle 400 Å in diameter, and a spherical particle 100 Å in diameter.[8] The concentration at the surface,

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[6] In the stationary state, the number of complexes crossing one *cm*² of a plane parallel with the surface at a distance x will be $-D\,dn/dx)$ per second, and this must be equal *to* the number of complexes in excess of n_0 vanishing per second in a column of one *cm*² cross-section extending from the plane outward to infinity. In symbolic form,

$$-D\frac{dn'}{dx} = \int_x^\infty kn'dx$$

differentiating

$$D\frac{d^2n'}{dx^2} = kn'$$

which gives on integration,

$$x = C_2' - \sqrt{D/k}\,\ln\left(n' + \sqrt{n'^2 + C_1/k}\right)$$

Now when $x = \infty$, $n' = 0$ and therefore $C_1 = 0$. Postulating that when $x = 0$, $n' = P'$ we get

$$n' = P'e^{-\sqrt{kx/D}}$$

[7] Starting with the same assumptions as in note 6, the number of complexes radiating from a particle and crossing concentric spherical envelope of radius r is

$$4\pi r^2 D\frac{dn'}{dr},$$

therefore

$$-4\pi r^2 D\frac{dn'}{dr} = \int_r^\infty kn'dv = 4\pi k\int_r^\infty n'r^2dr.$$

Differentiating

$$\frac{d^2n'}{dr^2} + \frac{2}{r}\frac{dn'}{dr} - \frac{k}{D}n' = 0.$$

The general solution is

$$n' = \frac{C_1}{r}e^{\sqrt{k/D}\,r} + \frac{C_2}{r}e^{-\sqrt{k/D}\,r}.$$

Now introducing the conditions that $n' = 0$ when $r = \infty$ and that $n' = P'$ when $r = r_0$,

$$n' = \frac{r_0}{r}P'e^{-\sqrt{k/D}\,(r-r_0)}.$$

[8] The radius of a cyboma containing 10 water molecules will be about 4.2×10^{-8} cm. Now from Stokes' law and kinetic theory.

$$D = \frac{RT}{6\pi\eta rN} = 5.2 \times 10^{-6},$$

where η is the viscosity of water (0.01), r the radius of the cyboma and N the number of molecules in one gram mole. From the assumption that the average life is 10^{-6}, $k = 10^6$, and

$$\sqrt{k/D} = 4.4 \times 10^{6}\ \mathrm{cm}^{-1} = 4.4 \times 10^{-3}\ \mathrm{A}^{\circ -1}.$$

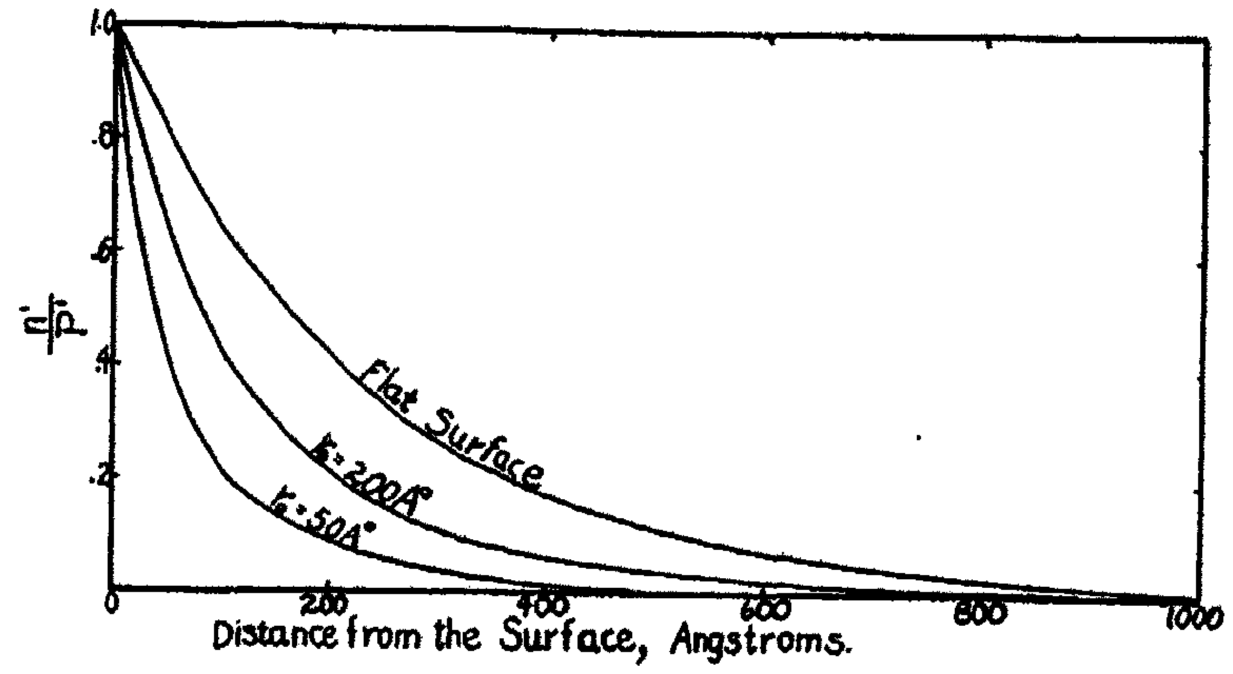

FIG. 2

Variation in concentration of cybomas with distance from flat and spherical lyophilic surfaces

P', is taken as unity. This value will undoubtedly be widely different for different surfaces. What its magnitude is can only be guessed, but it can easily be such that the diffusion pressure is that of a half molal solution. The influence of a surface at relatively large distances out into the liquid is strikingly shown by this figure.

Coagulation

A colloidal solution in which the micellar surfaces either decrease or do not affect the number of cybomas in their immediate neighborhood will be essentially unstable and will flocculate rapidly unless it can depend upon electric charge or some other means of keeping the particles from coming together and adhering. This is the case with the lyophobic colloids. If the concentration of the cybomas decreases with decreasing distance from the surface there will actually be a difference in the diffusion pressures due to the cybomas on the adjacent and far sides of two micelles near together, which will manifest itself as though there were an attractive force drawing the particles together. Fig. 3 represents this situation. That means that in such a sol the particles must have high electric charges in order to remain permanently dispersed. The addition of a small amount of precipitating ion, while not sufficient to neutralize the charge, may reduce it to the point where a particle of higher than average energy can penetrate through the electric atmosphere of another particle and adhere. This situation is strikingly parallel with that found in the typical lyophobic sols. The sols become unstable at Zeta potentials rather widely removed from zero. Also Smoluchowski[9] in the derivation of his familiar equation for rate of flocculation found it necessary to postulate the existence of an attractive force extending beyond the surface of a colloidal particle, although there has never been a satisfactory explanation of the nature of this force.

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[9] Physik. Z., 17, 557, 583 (1916); Z. physik. Chem., 92, 129 (1917).

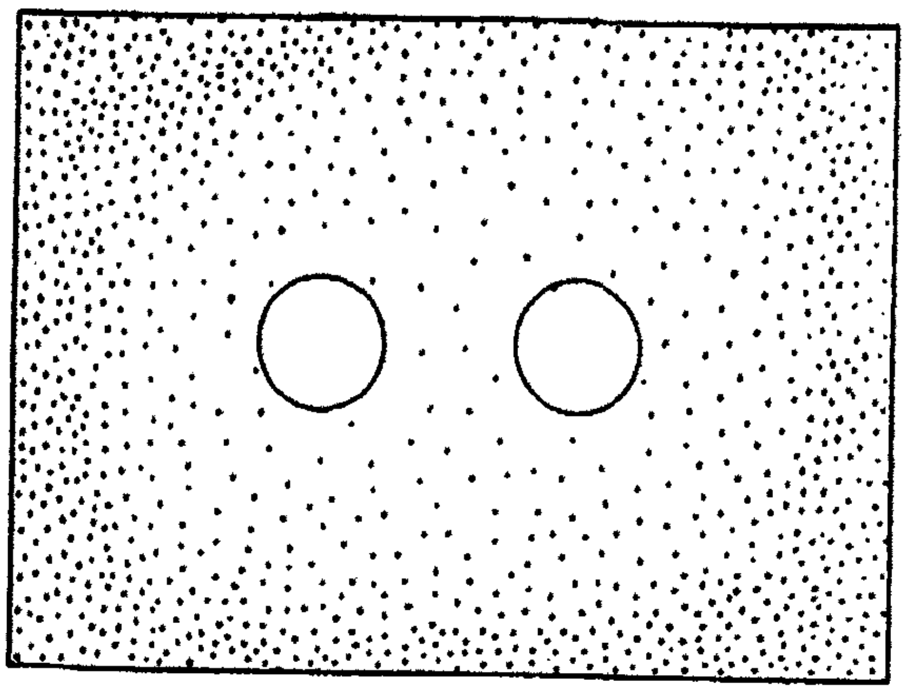

FIG. 3

Conditions surrounding two adjacent lyophobic particles, showing how they are forced together in the absence of electric charges.

Not only may an adsorbed substance affect the Zeta potential but it is highly probable that it also affects the relationship of the surface to the cyboma concentration. Thus it is possible that a sol that fits case (1) or even case (3) above may be so changed by the addition of an electrolyte or other substance that this attractive force will be brought into play and the sol will behave as a typical lyophobic sol. Such cases are rather common. For example, although aluminum oxide and vanadium pentoxide sols are classed among the hydrophilic sols, they are readily sensitized by various means so that very small quantities of electrolytes will precipitate them. The opposite may also be true and an added substance can very much increase the stability of a sol such as, for example, the addition of a protective colloid or the protective action of polyhydric alcohols on certain sols.

In the case where the concentration of cybomas in the immediate neighborhood of a micelle is considerably larger than that in the mass of the dispersing

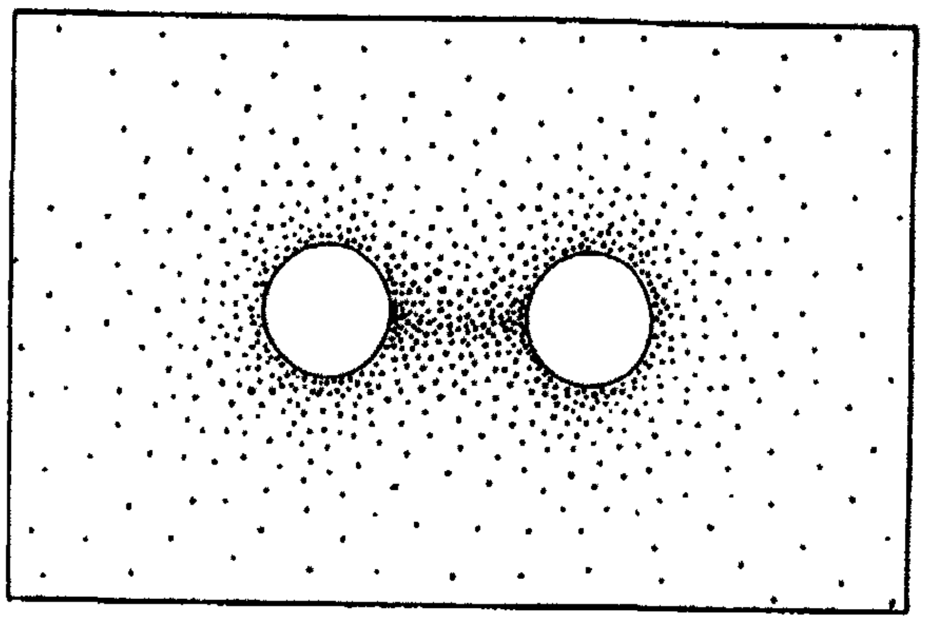

FIG. 4

Conditions surrounding two adjacent lyophilic particles, showing how cyboma pressure is built up between them.

phase, when two particles approach each other the conditions set up will be similar to that depicted in Fig. 4. There will be a decided increase in concentration of the cybomas in the region between the micelles which will have the effect of increasing the cyboma pressure on the particles and forcing them apart. The exact mathematical treatment of the rise in pressure on a micelle as it approaches another is very difficult, but it can be approximated by assuming that this rise in pressure will be proportional to the rise that would be produced if the micelle were surrounded by an envelope, of radius equal to half the distance between micelles, that is impervious to cybomas. In other words, all the cybomas produced by the surface would have to remain within this spherical envelope. Fig. 5 represents the effect of this envelope radius, R upon n′, the concentration of cybomas. In this figure $2(R-r_o)$ represents the distance separating the micelle surfaces and Π' the pressure at the surface when $R = \infty$, *i.e.*, when there is no interference with the outward diffusion of the complexes.[10]

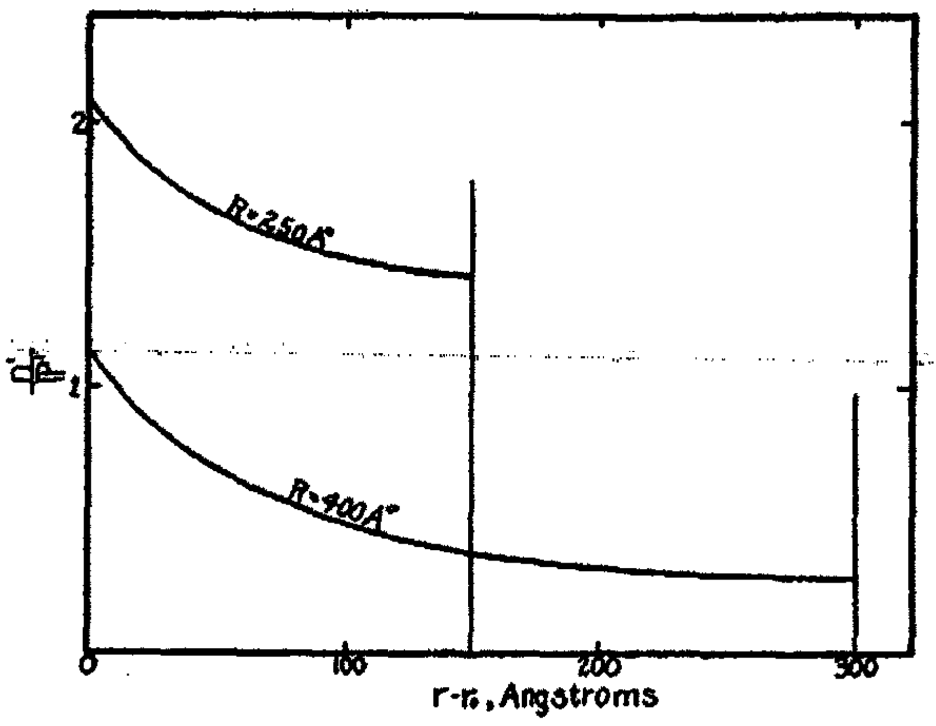

FIG. 5

The variation of n′ with distance from the surface of a spherical particle of radius 100 A° when the cybomas are prevented from diffusing beyond an envelope of radius R.

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[10] *Differentiating the general solution given in note 7, one gets*

$$dn'/dr = \kappa/r\,(c_1e^{+\kappa r} - c_2e^{-\kappa r}) - n'/r, \text{ where } \kappa = \sqrt{\kappa/D}.$$

Now where

$$r = R,\ dn'/dr = 0$$

$$c_1 = \frac{\kappa R + 1}{\kappa R - 1}c_2e^{-2\kappa R} \text{ and } c_2 = \kappa'' P'$$

where

$$\kappa'' = \frac{r_o}{\frac{\kappa R + 1}{\kappa R - 1}e^{\kappa(r_o - 2R)} + e^{-\kappa r_o}}.$$

Therefore

$$n' = \frac{\kappa'' P' \left\{\frac{\kappa R + 1}{\kappa R - 1}e^{\kappa(r - 2R)} + e^{-\kappa r}\right\}}{r}$$

and

$$\frac{P'}{\Pi'} = \frac{Kr_o + 1}{1 - K''K\left\{\frac{KR + 1}{KR - 1}e^{\kappa(r_o - 2R)} - e^{-\kappa r_o}\right\}}.$$

Fig. 6 shows the change of the ratio P'/Π' with changing values of R. Here P'/Π' represents qualitatively the repulsive force acting upon the side of the particle adjacent to another particle as compared to the normal pressure on the side discharging its complexes into free liquid. Here the existence of the equivalent of a repulsive force at large distances is illustrated. In Figs. 5 and 6 it is assumed that the rate of formation of cybomas at a surface is independent of P'/Π', which seems reasonable within limits.

As one can readily see, this pressure tending to force particles apart will give the sol stability without electric charge and this is the case with the typical lyophilic colloids such as gelatin or agar. With this type of colloid it can readily be seen from our picture that small concentrations of electrolytes will be relatively ineffectual in causing precipitation.

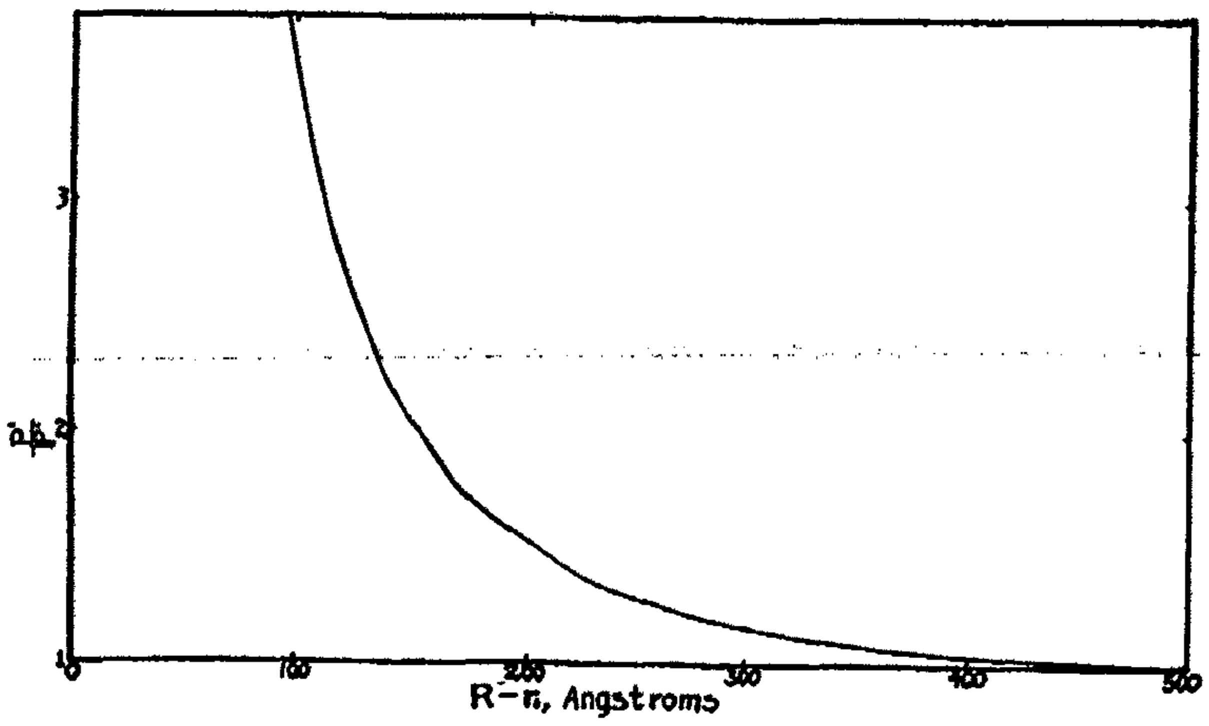

Fig. 6

The variation of the cyboma pressure on the surface of a particle of 100 Å radius produced by variation of the radius of an impermeable envelope.

From what has been said so far, it would be expected that lyophobic colloids would normally require some special means for dispersing them, while lyophilic colloids would tend to disperse themselves spontaneously, a difference which is one of the most characteristic of these two groups.

Again, the same picture that we have drawn would indicate that when rate of diffusion is measured by the diffusion of a sol along a concentration gradient, such as into pure water, the lyophilic particles should diffuse more rapidly than lyophobic of the same diameter due to this repulsion between the micelles with surfaces of type (3). This difference has been observed by Bruins,[11] who found that hydrophobic particles diffuse at the expected rate, while hydrophilic diffuse faster. Addition of electrolyte in the latter case decreased the rate, a fact easily explained on the basis of a decrease in the rate of complex formation at the surface. He also noted a parallel decrease in viscosity which is in complete harmony with this view, as will appear later. At first thought it

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[11] Kolloid-Z., 54, 265; 57, 152 (1931).

might appear that the electric field surrounding the lyophobic particles would produce the same repulsion at a distance as the cyboma cloud, but this is not the case due to the electric double layer, which although diffuse will reduce the repulsion between the particles to a negligible value at a relatively small distance.

The identification of lyophobic and lyophilic sols with types (2) and (3) respectively seems particularly logical since it would be expected that if there is an influence on the formation of cybotactic complexes by a surface, the surface more nearly chemically related to the solvent would be more apt to stimulate growth. In all cases of highly solvated colloids, the solvent and the colloid surface can be shown to be very similar in character. It may be that on solvated surfaces there is a distinct orientation of molecules that induces the orientation and addition of other neighboring liquid molecules upon it. Complexes grow outward from the surface, split off and others appear. Such a particle would appear like a large permanent cyboma seeding the surrounding liquid with its offspring.

Another prediction that comes directly from the interrelationship of the cybomas with a surface concerns the lyotropic series of monovalent cations. It is a common fact that with the more or less hydrophilic colloids such as aluminum oxide the precipitating power of these ions increases in the order $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow NH_4^+$, while there is practically no difference in their precipitating values with lyophobic sols. One of the most outstanding differences between these ions is the degree of hydration which decreases in the order given. The lithium ion is surrounded by a larger sphere of water molecules and perhaps by a larger number of cybomas than the other ions. The repulsion, therefore, between a lyophilic micelle and a lithium ion will be greater than between the same micelle and any of the other ions and, therefore, when equilibrium is established with a solution of definite concentration the amount of these ions adsorbed will be greater the lower the degree of hydration of the ion. In the case of the lyophobic particle, the establishment of equilibrium will be so much more dependent upon the charges than upon the hydration of the ions that this difference will have a negligible effect.

As two colloidal particles with lyophilic surfaces approach each other, there will be no repulsive force experienced by either as the cyboma clouds interpenetrate until sufficient time has elapsed for the new conditions between the particles to effect a rise in the concentration of the cybomas at the surface of the particle. This time lag means that the faster moving particles will be able to come much closer together before repulsion is experienced and therefore will have much better opportunities to come together and adhere. Since all particles on the average possess the same kinetic energy, the smaller micelles will move faster and have greater opportunities to attach themselves to others. This effect of size will be further accentuated by the fact that the smaller particles have less dense clouds of cybomas surrounding them as is shown by Fig. 2. This means that very small or very large particles in lyophilic sols will not be as common as some intermediate size, or in other words, the lyophilic sols will tend to have uniform particle size. It is possible that the pronounced uniformity of certain proteins may be thus explained.

The action of a protective colloid is readily understood in the present light. The particles of highly lyophilic colloid surround the lyophobic particle giving it a lyophilic character. Adsorption of the protective colloid can occur even though adhesive forces are negligible, due to the fact that when once the particle with its cyboma cloud has come into contact with the lyophobic particle, there will be a decided difference in diffusion pressure of the cybomas between the particles and on the outside, which will tend to hold them together.

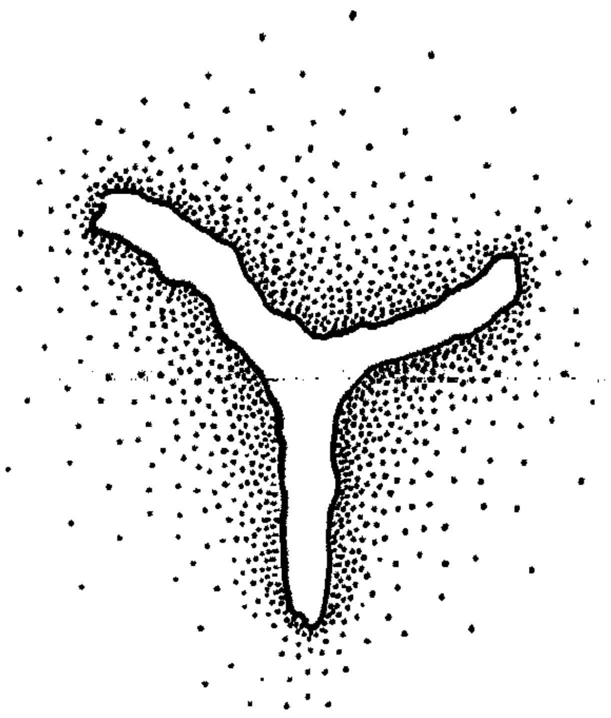

FIG. 7

Distribution of cybomas around an irregular lyophilic body, showing the much decreased density where the radius of curvature is small. Micelles can therefore most readily attach to edges and corners.

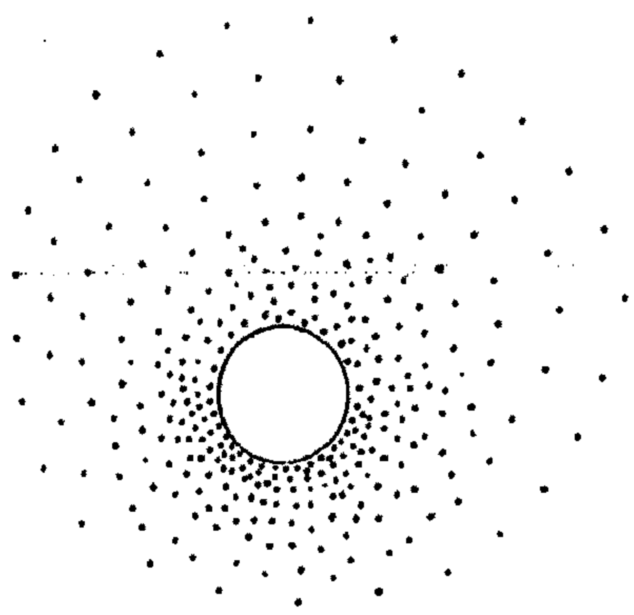

FIG. 8

Conditions surrounding a colloidal particle settling in a gravitational field illustrating the buoyant effect of the cyboma cloud.

The fact that the concentration of cybomas at a given distance from a solvated surface is smaller the smaller the radius of curvature of the surface leads one immediately to the conclusion that under circumstances in which agglomeration may occur, it will be easier for micelles to penetrate the cyboma cloud and attach themselves on edges and corners of a mass already coagulated. One, therefore, would anticipate that the agglomeration of such micelles would lead to the formation of chains, plates, or irregular fibrous or membranous structures rather than solid masses. The conditions surrounding an irregular mass would be somewhat as shown in Fig. 7. This type of structure would tend to surround and occlude large quantities of the dispersing medium and form a semi-solid spongy mass of practically the same volume as the original sol. Such a coagulated colloid we term a gel, and gel formation is one of the most characteristic manifestations of the lyophilic colloids. The strength of such a gel would depend upon forces of cohesion between micelles, as well as upon their shape and the structure of the agglomerated mass.

Probably the stronger the character (3) the stronger will be the gel, due to the more fibrillar structure. Notable exceptions occur to this rule—such as silica gel, in which the structure is probably not that of agglomerated colloidal particles but is, at least in part, due to what one might term dendritic crystallization.

An interesting possibility is that cyboma clouds surrounding large hydrated molecules such as those of sucrose may have a real influence in preventing crystal nuclei from forming in supersaturated solutions. It is logical that if they are present they will tend to hinder the proper orientation and close approach of sufficient molecules to form a stable crystal nucleus.

It is clear that a cloud of these evanescent molecular complexes surrounding a colloid particle will have a very decided influence upon its rate of sedimentation. As the particle settles through the liquid the complexes diffusing out from the lower side will be continually swept back toward the particle by the counter current of liquid, so that there will build up in the layer immediately in contact with the particle a higher concentration on the lower side and a proportionately lower concentration on the upper than normal. The conditions will be somewhat as represented in Fig. 8. The total effect will be as though a rigid sphere of liquid surrounding the particle were carried along with it. The particle will experience greater resistance than would be predicted by Stokes' Law.

Not only will this effect occur with particles falling in class (3) but it should manifest itself as well in case (2) because in this instance, the approach of cybomas to the lower side of the particle will be aided, while that to the upper side will be hindered and again a differential pressure on the two surfaces will be produced.

Viscosity

One of the most prominent features of colloidal solutions is their viscosity, which has been the subject of numberless investigations, but which as yet has received no adequate treatment. In view of the fact that viscosity of pure liquids itself has not been understood the failure to make marked progress with colloids is not surprising. Recently, however, Andrade[12] and Edwards and Stewart[13] have indicated the very close connection between the cybotactic complexes and viscosity, which intimates strongly that in this direction also lie large possibilities of application to the colloid field.

Accepting these authors' point of view, which is the most reasonable so far presented, it is evident that the fluid in a colloidal solution of the third type, that is, in which the number of complexes is increased due to the influence of the particle surfaces, will have a greater viscosity. This change of viscosity of the liquid will depend upon the surface character of the suspended particles. Its magnitude cannot at present be predicted, but will probably be small. Since it is a function of the total surface of the colloid, in sols of the same concentration but different particle size, it will be greater the smaller that size, which is one possible explanation of the variations that have been observed.

An influence of larger magnitude than that above will be that of the interaction of the cyboma cloud with the micelle. The same effect as that de-

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[12] Nature, **125**, 580 (1930).

[13] Phys. Rev., (2) **38**, 1575 (1931); Stewart: Nature, **128**, 727 (1931).

picted in Fig. 8 will come into play but in this case there will be two regions of increased pressure on opposite sides of the particle under shearing stress, as shown in Figs. 9, a and b. Fig 9, a, shows the effect of a low rate of shear in the liquid upon the cloud surrounding the micelle. Here the cloud is distorted and the resultant concentration on opposite sides of the particle will produce equal and opposite forces upon it directed at an angle with the plane of shear, the angle increasing with the rate of shear. These compressive forces will have resultants opposing the motion of the fluid so that the viscous drag of the particle will be greater than would be the case in the absence of the cloud. Fig. 9, b, shows the effect of a high rate of shear. It is hardly to be expected that the opposing force due to the distortion of the cloud will be a linear function of the rate of shear, but it seems probable that it will go through a maximum at high shearing rates. Compliance of a colloidal solution of type (2) or (3) with Newton's Law of the constancy of viscosity with rate of shear can, therefore, not be expected. The deviations will most likely be much greater with colloids of the third type. Again in this case the effect will be more pronounced with small particles than with large.

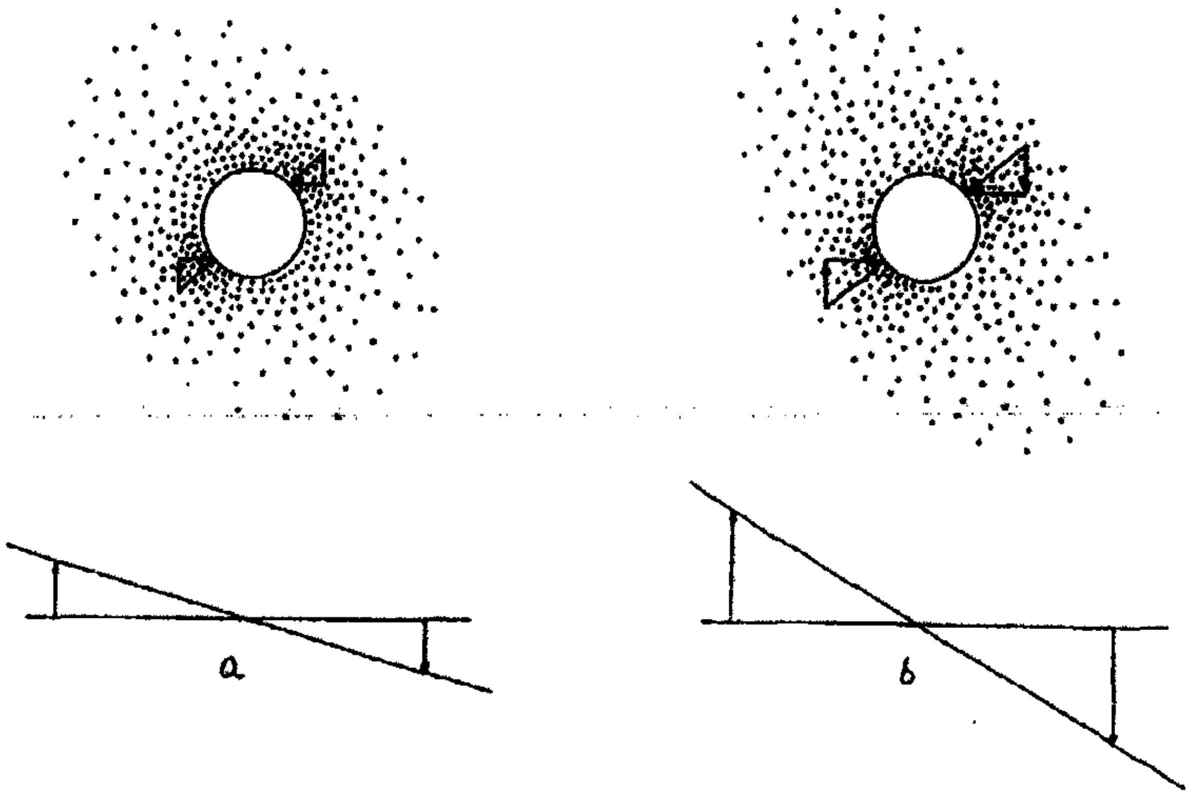

Fig. 9

A lyophilic particle under low and high shear showing how the cyboma cloud opposes the motion of the fluid.

The influence on viscosity just described will be independent of the existence of other particles in the solution. There is yet another influence on viscosity due to the proximity of the micelles and which will doubtless have the greatest effect in concentrated sols. As two particles pass each other in a sol under shear, the clouds surrounding each will interpenetrate and produce repulsions which can greatly increase the viscous drag, both due to the parallel components of the forces and to the fact that the particles will describe lengthened paths around each other. Fig. 10, a, represents schematically the interactions of two particles as they approach at low rate of shear. It will be remembered, from what has been said earlier, that the repelling force will depend upon disturbance of the equilibrium at the surface of a particle and, therefore, there will be a lapse of time between the penetration of the outer parts of the clouds and the development of the repulsion. The work required to move one particle past the other at a given distance will, therefore, diminish with increasing velocity of the particle. In addition, the extent of the cloud in the direction of the other particle will be reduced by rate of shear as shown in Fig. 10, b, so that at high rates of shear, the particles can approach much closer to each other, and they will be more nearly opposite before experiencing repulsion, so that the viscous drag will be much less at high shearing rates than at low. This difference in affect of rate of shear can be easily seen by comparing Figs. 10, a and b.

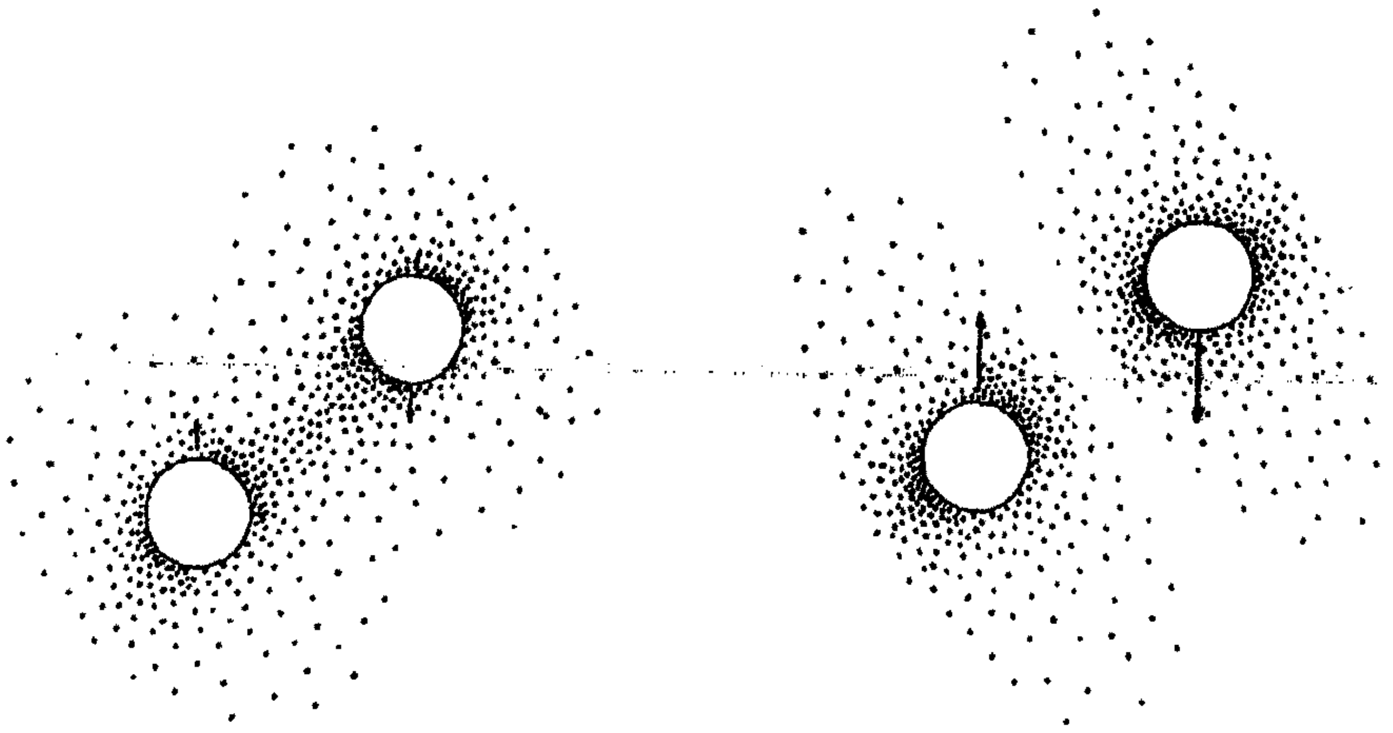

Fig. 10

a b

Two lyophilic particles passing at low and high shearing rates. The effect of rate of shear upon the mutual interference of the particles is clearly seen.

It might be assumed that as the particles pass each other at high shear and the distorted clouds intermingle there will be a repulsive force which will contribute to their progress and thus tend to decrease the viscous drag. Fig. 11 shows such a case. However, upon more careful consideration of the conditions existing in Fig. 11, it is evident that these distorted sections of the clouds intermingling are being swept away from the particles so that, although there will be a region of greater density of the cybomas between the micelles, the time lag previously mentioned will prevent any appreciable concentration effect at the micelle surfaces before they are swept out of range.

As would be gathered from examination of Figs. 5 and 6, this viscous effect depending on the proximity of the particles should increase rapidly with increasing concentration, and also at constant concentration should increase with decreasing particle size. The latter effect being due to the much smaller average distances between the small particles.

From what has gone before it is to be concluded that a decrease in particle size will inevitably lead to an increase in viscosity in all solutions of type (3), and probably also of type (2) since the interactions of the particles will probably play a more important rôle than the effect on the total number of cybomas in the liquid. Experimental results such as those of Odén[14] on sulphur sols lend support to this prediction.

Double Refraction of Non-Spherical Particles

From general considerations it would be predicted that the optical axis of non-spherical particles suspended in a liquid under shear would coincide with the plane of shear, but this has been found to be the case only with coarse dispersions. In most cases that have been investigated the axis lies at an angle between 0 and 45° with the plane. With elastic solids and jellies the angle is 45°. There has been no adequate explanation of the failure of the particles to orientate themselves completely in the plane of shear and statements such as the following from Kraemer[15] have received widespread if tentative acceptance. "The particles in the sols mentioned seem to be united in some way, forming a more or less tenuous, elastic structure that undergoes deformation as well as orientation."

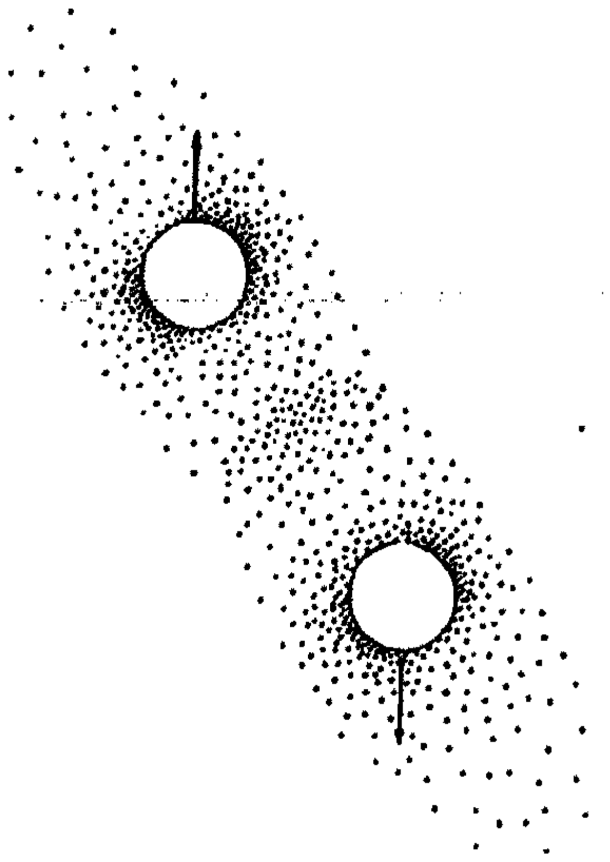

FIG. 11

Conditions existing after two particles under shear have passed.

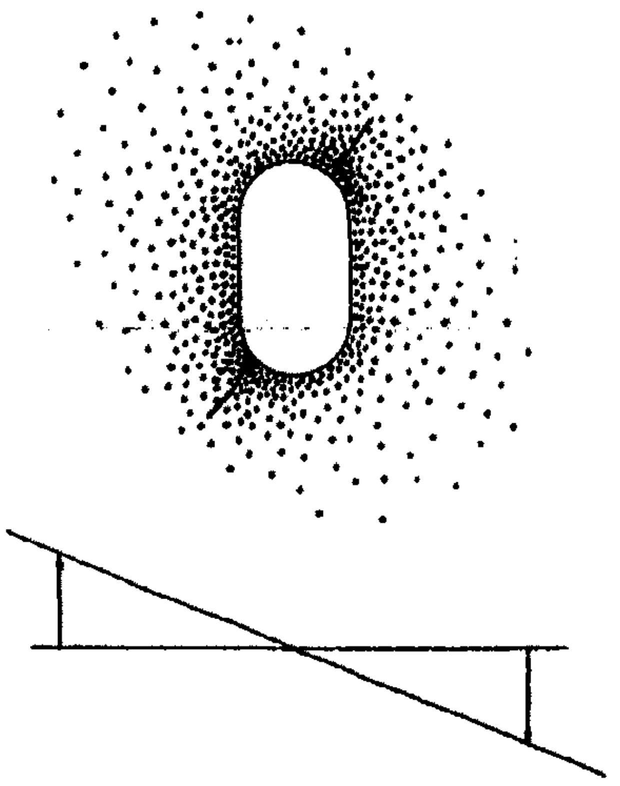

FIG. 12

Illustration of the unbalanced forces acting on an elongated particle lying in the plane of shear. The necessity for rotation of the axis out of the plane of shear is shown.

An orientation of non-spherical particles at an angle with the plane of shear arises out of necessity from our hypothesis of the conditions surrounding

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[14] Z. physik. Chem., 80, 709 (1912).

[15] Kraemer: "Treatise on Physical Chemistry," Edited by Hugh S. Taylor, 2, 1609 (1931).

(The first person to postulate this connection between orientation and elastic deformation seems to have been Pontremoli: Atti Accad. Lincei, 30 II, 216 (1921).).

a particle of type (2) or (3). Referring to Fig. 9, a or b, one will immediately see that in case the particle is elongated, the forces acting upon it from opposite sides will no longer be balanced and there will be a rotation of the particle to a new position at an angle with the stream. This unbalanced condition can more readily be visualized by reference to Fig. 12. The particle will rotate in a direction away from the approaching current and the extent of rotation will be less the more elongated the particle is. With increasing rate of shear the angle of deviation should be reduced since the viscous drag on the surface is in such a direction as to oppose the orientating forces.

Freundlich, Neukircher, and Zocher[16] have carefully measured the optic axis of several non-spherical sols and their results confirm completely the predictions made above. For example, the angle is found to decrease with age of a vanadium pentoxide sol, while the length of the particle increases. The angle decreases with increasing rate of shear and its direction with respect to the motion of the liquid is what has been predicted. While their offered explanation based on the existence of swarms of micelles can in no way be said to be invalidated, certainly the explanation based on the influence of the cybomas seems to involve less artificiality.

It does not longer seem to be necessary to postulate the existence of elastic forces acting at relatively great distances throughout the sols.

Thixotropy

In sols of type (3), it is evident that particles will tend to take up positions at maximum distances from each other, which means that barring other disturbances, a quiet sol will assume a definite structure. Any small force tending to destroy this structure will be met by a quasi-elastic resistance, and if the disturbing force is quickly enough withdrawn, there will be elastic recovery from the deformation. Such elastic resistance must be met due to the fact that when the micelles are in the configuration of maximum distance from each other, any small deformation must reduce this distance, thus increasing the forces between certain of the micelles in a direction which would oppose the disturbance.

Even in the absence of Brownian movement, the opposing force, induced by a small deformation, would gradually sink to zero due to the migration of the particles to new optimum positions, a phenomenon which resembles closely in external aspects relaxation under stress in elastic solids.

The presence of Brownian movement will naturally hinder the complete orientation of the micelles into optimum positions, so that the higher the temperature, other things being equal, the less distinctly will the elastic properties manifest themselves. Since the repelling forces between particles rise rapidly with increase in concentration, a concentrated sol may show a definite yield point, whereas a more dilute sol may be sufficiently disturbed by Brownian movement so that no yield value can be obtained even at very low rates of shear. In the more concentrated sol, the shearing stress will approach a con-

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[16] Kolloid-Z., 38, 43, 48 (1926).

stant value with decreasing rate of shear as shown by Curve 1, Fig. 13, while in the dilute sol, due to the rapid relaxing affect of the Brownian motion, no limiting value of shearing stress will be approached but as the rate of shear becomes very small, the shearing stress will drop off in the manner of Curve 2, Fig. 13. These two curves will be recognized to be very typical of lyophilic colloidal solutions.

Again decrease in particle size will manifest itself in a direction similar to increase in concentration, since, although Brownian disturbances will increase with decreasing particle size, the intermicellar forces will increase more rapidly.

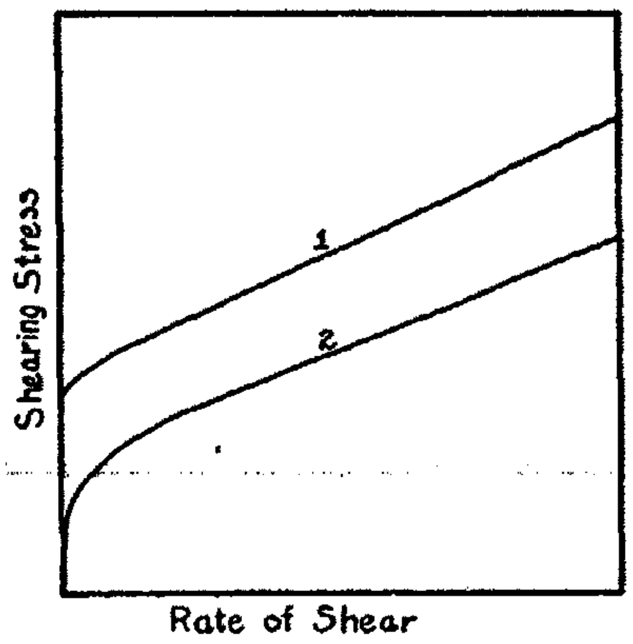

FIG. 13

Typical stress-rate of shear curves for sols. Curve 1 shows a definite yield point while 2 shows none.

The influence of concentration upon the yield point cannot be exactly given, but in the simplified case where Brownian movement is assumed to be negligible, it seems justifiable to assume that each particle is surrounded by practically a sphere of other particles, i.e., it is circumscribed by a spherical envelope where $dn'/dr = 0$, the conditions assumed for Figs. 5 and 6. The yield point of the sol should therefore be approximately proportional to dP'/dR, since the restoring forces after a disturbance will be proportional to the same quantity. Taking R as proportional to the cube root of the volume, the variation of yield point with volume of sol should be somewhat as shown in Fig. 14 for particles of 100 Å radius. From this figure one would certainly anticipate evidence of yield point in sols of small particle size when the volume of colloid is greater than 10% of the total volume.

Due to the time required for the forces to produce optimum orientation, a lyophilic sol that has been thoroughly mixed will show a rise in viscosity with time. On the other hand, if the sol is allowed to stand quiescent in a viscometer and then its viscosity is measured at constant rate of shear, it will be found to decrease with time and extent of working to some constant value which, however, will be smaller the greater the rate of shear, due to the smaller opportunity for the repelling forces to set up the ordered arrangement.

This rise in viscosity with quiescence and return again upon working, particularly when the sol develops a definite yield value upon standing, has been termed thixotropy. Several tentative explanations have been proposed for it but none have been found satisfactory, and it was in a search for a satisfactory explanation that the author was led to a consideration of the influence of cybotactic complexes.[17]

Although the explanation as given seems to account successfully for numerous observations, it does not seem to me that the yield value described above

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[17] Kistler: J. Phys. Chem., 35, 828 (1931).

can have the magnitude of that found in certain thixotropic gels, such as those of Fe_2O_3 and Al_2O_3. In these cases, probably reversible coagulation plays a part. These gels belong to the class in which a decided Zeta potential is necessary for stability, and it may be that upon the addition of the small amount of electrolyte necessary to bring about the thixotropic condition, the surface is changed to type (2) in which there is a definite attraction between particles. Since this attractive force undoubtedly extends farther than the electric repulsion there will be a tendency for the particles to take up positions with respect to each other at a smaller distance than the average distance of separation of the particle in the sol. Under such circumstances the particles in a quiescent sol will tend to collect into flocks which may be irregular and tenuous. Within each swarm of micelles the particles would tend to assume very definite positions with respect to each other in which the attractive forces would be counter balanced by the electric repulsions. Since the average distance separating the particles in any one swarm would probably be small due to the limited extent of the electric fields, the swarm could possess considerable rigidity. Since the micelles forming any swarm must be drawn from the liquid in the immediate neighborhood, the swarms must necessarily be small in cross section but may be inter-connected so that they form in effect an anastamosing sponge-like structure extending throughout the whole volume of the sol. Such a structure when completely formed could give the sol a rigidity much greater than it could possess if the particles remained dispersed at maximum distances. This two-phase sol would assume the aspects of a gel but would again become a mobile liquid upon mechanical agitation and dispersion of the swarms.

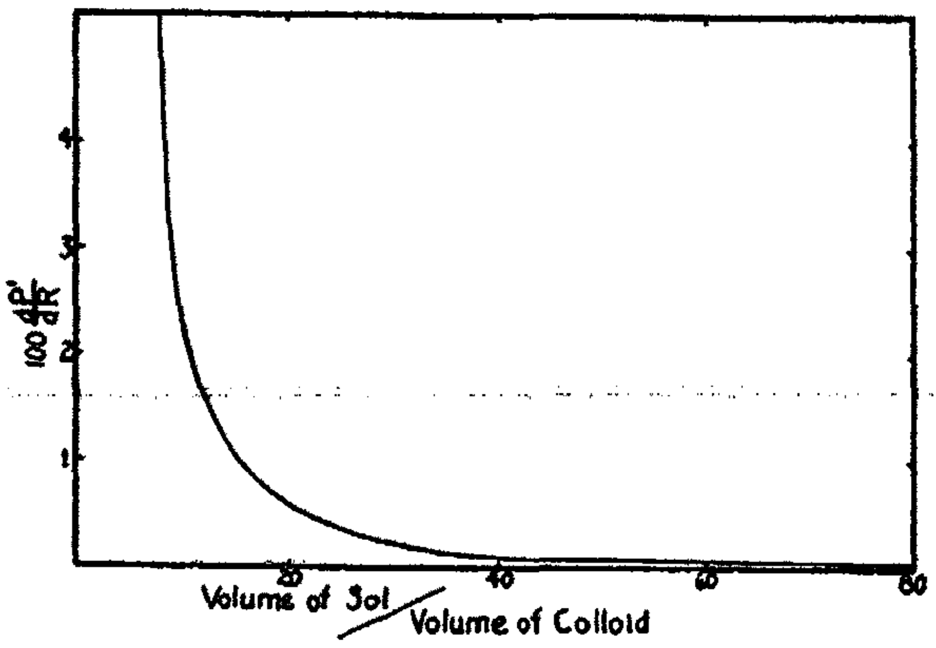

FIG. 14

Curve illustrating the probable influence of the dilution of a lyophilic sol upon the yield point.

If the above explanation of this particular type of thixotropic sols is correct, one would expect that the thixotropic condition would occur only in a very limited range of electrolyte concentration. Occurring as a balanced condition between electric charge and attractive force one should expect that only certain sols would be capable of attaining this balance. In general, the sols of type (2) would coagulate rather than halt on this metastable plateau. These expectations have been realized and although it may become possible to induce thixotropy in many more sols, at present the number of electrolyte-sensitive sols that have been brought into this condition is relatively small.

Such swarms of particles as have been postulated above have been demonstrated to exist in aged V_2O_5 and Fe_2O_3 sols.[18] Zocher has applied the term "tacto-sols" to these swarms. Those that he has studied have shown a definite optic axis which indicates that the particles are non-spherical and orientated. The orientation, there observed, would be a natural consequence of formation as above postulated.

Although the theory of the influence of cybotactic complexes upon colloidal systems as presented above, offers, in itself, an explanation of a large number of phenomena, I do not wish to imply that it is the sole cause of these phenomena, but that it is a general background upon which may be superimposed other effects which have been given credence in the current literature.

It is a pleasure to acknowledge my indebtedness to Dr. David G. Bourgin, Mathematic Department, University of Illinois, for his assistance in deriving and checking the formulas used, and to Professor H. Freundlich, Berlin, for carefully reviewing the manuscript before its presentation.

Summary

1. The existence of cybotactic complexes in liquids is discussed and it is shown that colloids may be divided roughly into two classes, corresponding to lyophobes and lyophiles, depending upon whether the surfaces tend to depress or stimulate the formation of cybotactic complexes, called here "cybomas."

2. The stability of a lyophilic sol is shown to depend mainly upon a concentration gradient of cybomas decreasing with distance from each colloid particle, while the tendency to coagulate and the previously postulated force of unknown origin tending to draw particles at a distance together in lyophobic sols are connected with a gradient of opposite sign.

3. Reasonable assumptions are made in regard to the average size and average life of cybomas, and equations derived showing the relatively great distance into a liquid at which a surface may have influence.

4. The differences between ease of dispersion of lyophile and lyophobe colloids, and the unexpectedly large rate of diffusion of the former are explained.

5. An explanation of the lyotropic series $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow NH_4^+$ is given.

6. The fact that lyophilic sols tend to possess very uniform particle size is predicted from the interactions with cybomas.

7. The tendency shown by lyophiles to precipitate in fibriles, plates or "brush heaps" enclosing much liquid is shown to be a necessary consequence of the assumptions made.

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[18] Zocher: Z. anorg. Chem., **147**, 91 (1925); Zocher and Jacobson: Kolloid-Z., **41**, 220 (1927); Kolloidchem. Beihefte, **28**, 167 (1929).

8. A probable influence of cybomas on the tendency of large hydrated molecules such as sucrose to supersaturate is indicated.

9. The influence of a colloid on the viscosity of a liquid is ascribed to three separate affects, (a) the influence on the total number of cybotactic complexes, (b) the interaction between these complexes and a particle under shear, tending to increase the resistance offered by the particle to viscous flow, and (c) the interactions between two particles while passing, due to intermingling of their attendant cyboma swarms. It is pointed out that the particle size of lyophiles must have a large influence on viscosity, the smaller the particles the greater the viscosity.

10. The fact that nonspherical particles do not orient themselves in the plane of shear is shown to arise of necessity from the adopted assumptions, and the direction of rotation as well as the influence of rate of shear and particle size are predicted.

11. The failure of a lyophilic sol to show constant viscosity with different rates of shear, the rise in viscosity with decrease in shearing rate, the decrease of viscosity with time at constant rate of shear, and the existence of a yield point are predicted. In other words, thixotropy is given a rational explanation.

12. A reasonable explanation is offered for Zocher's "tacto-sols."

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THE ADSORPTION OF ELECTROLYTES BY ASH-FREE CHARCOAL

VII. A Brief Survey of the Present Status of the Subject, and Evidence that Negative Adsorption of Inorganic Bases decreases with Length of Time of Contact of Charcoal with Solution*

BY ELROY J. MILLER

At the Fifth Colloid Symposium[1] a summary was presented of the studies that had been carried out on adsorption from solutions of acids, bases and salts by adsorbent charcoal. It was pointed out that the earlier results obtained by Freundlich, Michaelis, Odén, and others in their adsorption studies with blood charcoal were anomalous and contradictory. In the light of the results obtained with activated sugar charcoal and other ash-free charcoals, these discordant results could be satisfactorily explained on the basis of impurities in the charcoal such as ash, incompletely decomposed organic matter, and unsuspected adsorbed acids. The results with the ash-free sugar charcoal, and with the purified charcoals of animal and vegetable origin, were surprisingly consistent and reproducible, and many new facts were established which since that time have been verified in a number of laboratories. Adsorption from solutions of electrolytes seemed to be on a firm basis and the groundwork was indeed laid for many future investigations, as is evidenced by the scores of papers that have appeared on the subject since that time. It seems desirable again to present a brief survey of the present status of the subject.

It will be recalled that ash-free adsorbent charcoal that has been heated at temperatures around 1000° has the property of adsorbing acids, but it does not adsorb the inorganic bases.[2] From many salt solutions the charcoal adsorbs acid hydrolytically with the liberation of alkali. Ash-free charcoal adsorbs large amounts of acids such as benzoic and salicylic. Dicarboxylic acids such as succinic, malic and tartaric are moderately adsorbed. Adsorption of aliphatic acids increases with increasing length of carbon chain. Inorganic acids, such as HCl, H_2SO_4 and HNO_3, are relatively slightly adsorbed. Inorganic bases are not adsorbed at all. The introduction of polar groups such as hydroxyl and amino groups into organic acids decreases adsorption. In the aliphatic acid series the shorter the carbon chain the greater is the effect of the introduction of the polar groups. Thus the introduction of the amino group into acetic acid cuts down the adsorption completely. Furthermore, the position of the polar groups in the molecule influences the adsorbability of the acid. O-, m- and p-hydroxy benzoic acids and o-, m- and p-amino benzoic acids are adsorbed in different amounts depending upon the position of their polar groups; the ortho acid is adsorbed most, the para next and the meta least. Isomeric forms of the fatty acids, butyric, valeric and caproic are adsorbed less

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* Contribution from the Chemical Laboratory of the Michigan Agricultural Experiment Station. Published with the permission of the Director of the Experiment Station as Journal Article No. 122 (n.s.)

than the normal forms. It should be particularly noted that while NH_4OH is not adsorbed at all, tetramethylammonium hydroxide is slightly adsorbed and tetraethylammonium hydroxide is quite appreciably adsorbed. It is interesting and significant that these organic bases which are practically as strong bases as are NaOH and KOH are positively adsorbed, whereas the latter are not adsorbed at all or are actually negatively adsorbed.

Complete Proof of Hydrolytic Adsorption

Methods were developed for the quantitative estimation of adsorbed acids on ash-free charcoal.[3] Known amounts of acids were adsorbed on charcoal and the amounts of acid recovered were quantitatively equal to the amounts adsorbed for various types such as aromatic, dicarboxylic, aliphatic and inorganic acids. With the development of these methods for the quantitative estimation of adsorbed acids on charcoal it became possible to furnish complete proof of hydrolytic adsorption. The amount of alkali set free by the charcoal was determined and the charcoals were then examined for the presence of adsorbed acids. The results with salts of a number of organic acids showed that the amount of adsorbed acid recovered from the charcoal was exactly equivalent to the alkali set free and left in solution. Similar results were obtained with salts of inorganic acids, but in addition, the chloride and sulphate were determined and also found to be equivalent in amount to the acid adsorbed and base set free. Complete proof of hydrolytic adsorption from salt solutions was thus established. The charcoal contained no alkaline impurities, and the acid recovered from the charcoal was the same as that from which the original salt had been derived.

Hydrolytic and Molecular Adsorption from Salt Solutions

From an investigation of adsorption from a series of potassium salts[4] it was found that the hydrolytic adsorption from solutions of inorganic salts was exclusively hydrolytic, while from salts of organic acids, adsorption was both hydrolytic and molecular. The concentration of potassium after adsorption had decreased in solutions of salts such as potassium benzoate and salicylate, indicating that besides hydrolytic adsorption of acid from the salt, there was adsorption of the salt as such. The concentrations of potassium in solutions of potassium sulphate, nitrate, and chloride were actually slightly higher after adsorption, indicating that only acid (and some water) was adsorbed from these solutions. It was evident from other facts that the increase in concentration was undoubtedly due to adsorption of water along with the acid hydrolytically adsorbed. It was observed that while the adsorption of the inorganic salts was exclusively hydrolytic the absolute amount of potassium hydroxide set free was approximately only one-fourth that set free from sodium benzoate.

Negative Adsorption of Potassium Hydroxide

By the use of larger quantities of charcoal (10 grams or more) it was definitely established[4] that negative adsorption of potassium hydroxide occurs.

The concentration of potassium after adsorption was higher than in the original solution, but the absolute amount of potassium was the same before and after adsorption. These results on negative adsorption were all obtained under uniform conditions. The charcoal was always freshly ignited just before use and allowed to remain in contact with the solution for a definite length of time. It was found, however, that when these conditions were varied the resultant effects were not always in agreement.

Decrease of Negative Adsorption with Time

It was surprising to find (Table I) that the length of time the charcoal and solution remained in contact determined very largely the magnitude of the negative adsorption. And still more surprising was the fact that the magnitude of the negative adsorption, contrary to positive adsorption, decreased with time, and fairly rapidly. Thus in one experiment, at the end of thirty minutes 3 cc. of water had been adsorbed while at the end of twenty-six hours the value had decreased to 0.6 cc. In another experiment, at the end of fifteen minutes 2.9 cc. of water had been adsorbed and at the end of twenty-six hours the value had decreased to 0.1 cc. The results were somewhat erratic, however, and it was evident that not all the controlling factors were known. From

TABLE I

Decrease of Negative Adsorption of NaOH with Time

14 g. Ash-Free Blood Charcoal (Old Type, 1925)
added to 100 cc. 0.02 N NaOH

Duration of Contract	Cc. 0.02 NaOH Adsorbed
5 minutes	−1.9
20 "	−1.4
35 "	−0.6
3 hours	+0.3
48 "	+1.8

9 g. Ash-Free Blood Charcoal (Old Type, 1929)
added to 100 cc. 0.02 N NaOH

30 minutes	−3.00
30 "	−3.52
25 hours	−0.60
70 "	−0.60

9 g. Ash-Free Blood Charcoal (Old Type, 1930)
added to 100 cc. 0.02 N NaOH

20 minutes	−2.30 (2)
20 "	−2.30 (4)
75 "	−2.90 (1)
43 hours	−0.10 (5)
53 "	−0.30 (3)

a considerable number of experiments (Fig. 1), however, it was quite evident that negative adsorption does decrease with time. When the adsorption effects were measured within thirty minutes after addition of the charcoal to solution, a considerably higher value for the water adsorption was obtained than when charcoal and solution remained in contact for a period of twenty-four to seventy hours. In a few instances positive adsorption appeared to be indicated, but it was later found that these were undoubtedly due to the fact that the temperature of ignition was too low, and substances of an acid nature had been formed on the charcoal.

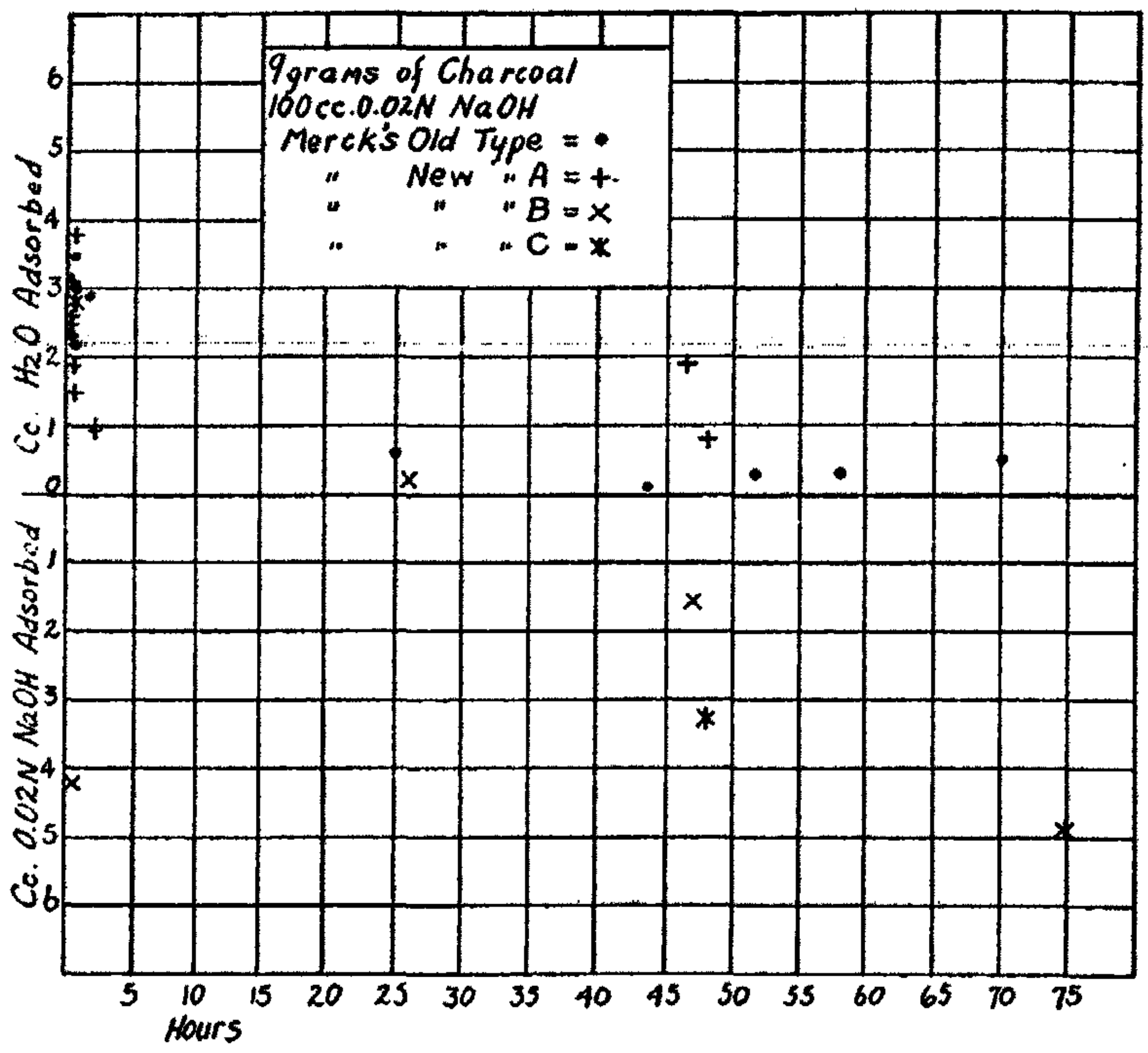


FIG. 1

Decrease of Negative Adsorption with Time of Contact of Charcoal with Solution

Effect of Temperature of Ignition of Charcoal on Adsorption from Solutions of Sodium Hydroxide

An investigation of the temperature factor (Table II) definitely indicated that the temperature to which the charcoal is heated prior to the adsorption does influence the results. For example, the charcoal sample No. 4 when heated in the neighborhood of 1200° at the end of thirty minutes gave a negative adsorption of 1.95 cc. and at the end of two hours 0.96 cc., but when heated at 500° a marked positive adsorption of sodium hydroxide was observed. After washing, drying and re-igniting at 1200° negative adsorption was again obtained. When again heated at 500° negative adsorption was still observed. The fact that the second heating at 500°, gave a negative adsorp-

TABLE II

Effect of Temperature of Ignition of Charcoal on Adsorption of NaOH
9 g. Ash-Free Blood Charcoal (New Type) added to 100 cc. 0.02 N NaOH

Charcoal Sample	Temperature of Ignition	Duration of Contact	Cc. 0.02 N NaOH Adsorbed
No. 1	900°	30 minutes	+1.76
"	900°	30 "	+0.20
"	900°	30 "	−0.40
No. 2	900°	24 hours	+7.96
"	900°	30 minutes	+0.56
No. 3	900°	72 hours	+1.86
"	900°	30 minutes	+0.80
No. 4	1075°-1200°	2 hours	−0.96
"	1075°-1200°	30 minutes	−1.96
"	500°	20 "	+8.00
"	1200°	20 "	−3.10
"	500°	15 "	−2.60
"	1200°	47 hours	−1.90
"	1200°	20 minutes	−2.50
"	1200°	48 hours	−0.80

tion while the first heating gave a positive adsorption could not easily be explained at first, but Kruyt and de Kadt[5] published a note somewhat later which afforded a simple explanation for the apparent discrepancy. They found that charcoal which had been heated at 900° and which adsorbed acids but not inorganic bases was reheated at 400° in oxygen, it acquired the property of adsorbing bases. This property could be destroyed by again heating at the higher temperature.

Kruyt and de Kadt postulated the formation of substances of an acid nature such as intermediate products of mellitic acid on the surface of the charcoal by the heating in oxygen at lower temperatures. At the higher temperature the acid substances were destroyed. These acids could easily account for the apparent adsorption of bases as had been repeatedly shown[1] for adsorbed acids on ash-free charcoal. For example, an ash-free charcoal heated at 1075° adsorbed a large amount of benzoic acid but no sodium hydroxide. When complex water-insoluble methyl red acid was adsorbed on the charcoal it was able to take up a considerable amount of alkali (molecular adsorption of salt of strongly adsorbed organic acid), and when the charcoal was reheated at 1075° to destroy the methyl red acid, the charcoal no longer took up any alkali, but still adsorbed benzoic acid. Kruyt's charcoal and charcoal carrying adsorbed organic acids then have properties in common.

The apparent discrepancies in the behavior of the charcoal after various heat treatments were eliminated when it was found necessary to heat the charcoal above 900° for a considerable time in order to completely decompose the acid formed on the charcoal. Once the charcoal has been freed from the carbon acids, however, heating at 500° in the absence of air does not result in the formation of the acid, and negative adsorption of alkalies which decreases with time is still observed. For rapid formation of the complex acid it is necessary to heat the charcoal at 300-400° in the presence of air and water vapor, although the action takes place slowly even at room temperature.

Recently, Kolthoff[6] has attempted to obtain more information on the nature of the acid formed on the surface of Kruyt's charcoal and found evidence of the formation of a complex colloidal acid. If taking up of alkali by Kruyt's charcoal is the same as adsorption of acid, then the 400° charcoal should adsorb KOH hydrolytically from KCl with the liberation of HCl, but Kolthoff could not detect any liberation of HCl and indeed the chloride content of the solution after adsorption had decreased slightly. The solution had become slightly acid, however, and Kolthoff found some evidence of the presence of a complex colloidal acid.

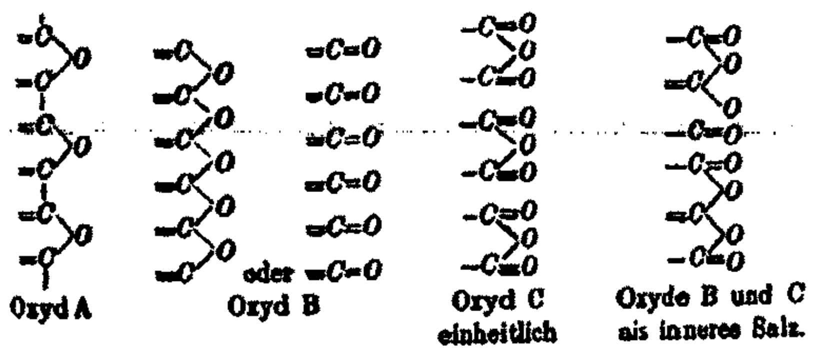
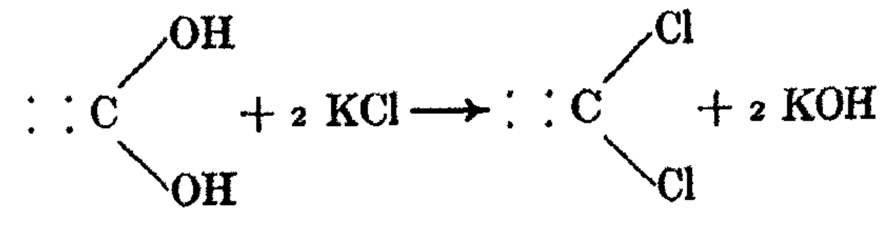


Fig. 2
Schilow's Oxides of Carbon

Schilow's Oxide Theory

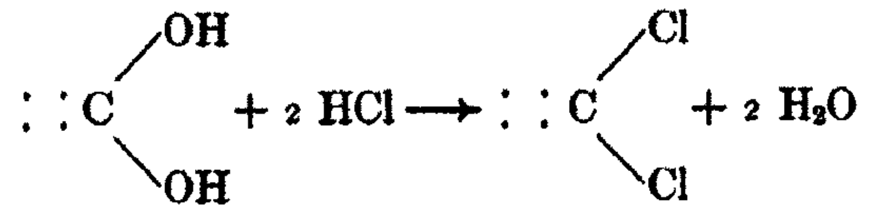
About the time that Kruyt and de Kadt made their discovery, Schilow and co-workers[7] also observed that charcoals heated at lower temperatures took up bases. From this and other facts they postulated a theory that adsorption of acids, bases and salts by charcoal takes place through interaction with acidic and basic oxides of carbon on its surface. Schilow[8] pictures these oxides (Fig. 2) as A which with water gives a slightly basic carbon hydroxide, oxide B which forms a strongly basic hydroxide and oxide C which is acidic in nature. An inner salt of oxide B and C is also pictured. Oxide A is stable at all temperatures and in presence of oxygen up to 2 mm. pressure. Oxide B is formed from A at 2 mm. oxygen pressure and is stable up to very high pressures. Oxide C is formed from oxide B by heating in oxygen at 300-700°.

Schilow's explanation of the mechanism of hydrolytic adsorption is as follows:



$$\vdots\, C\begin{matrix}\diagup OH\\ \\ \diagdown OH\end{matrix} + 2\,KCl \longrightarrow \vdots\, C\begin{matrix}\diagup Cl\\ \\ \diagdown Cl\end{matrix} + 2\,KOH$$

The chloride ion of the KCl replaces the OH ions and KOH remains in solution. Hydrochloric acid would of course react with oxide B to leave water in place of KOH, while potassium hydroxide would not react at all with it.



$$: : C(OH)_2 + 2\,HCl \longrightarrow : : C(Cl)_2 + 2\,H_2O$$

Schilow[9] found also that the oxygen pressure on the charcoal influenced markedly the adsorption of hydrochloric acid. In Fig. 3 are his curves for the adsorption of hydrochloric acid in a number of concentrations as affected by the oxygen pressures. The action is stepwise and independent of the adsorption isotherm for oxygen. At pressures up to 2 mm. the curves are horizontal, then there is a sharp break followed by another horizontal section. The lower section represents the adsorption by oxide A and the steep part marks the formation of oxide B, and the second flat part the adsorption by oxide B.

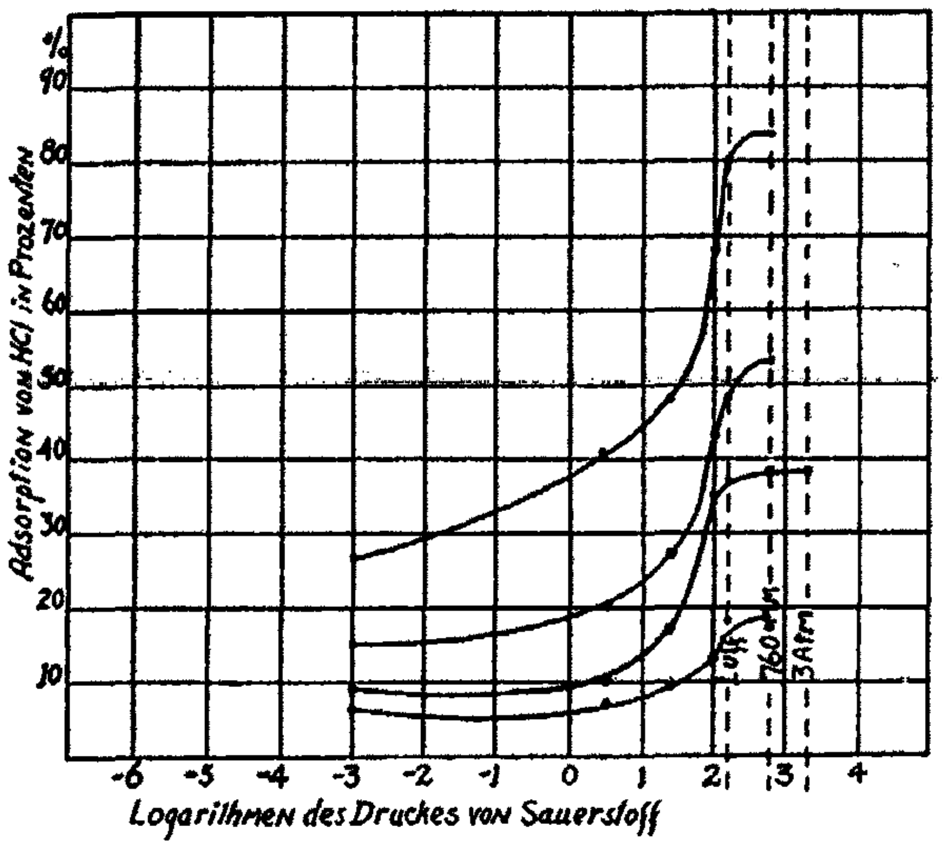


FIG. 3

Schilow's Curves for Adsorption of HCl against Oxygen Pressures

Frumkin's Gas Electrode Theory

Frumkin and co-workers,[10] however, obtained entirely different results for the relation between oxygen adsorbed and hydrochloric acid adsorbed. They found that within certain limits the milliequivalents of hydrochloric acid adsorbed were equal to the milliequivalents of oxygen adsorbed. Their curve for oxygen adsorption (Fig. 4) against pressure was smooth, and the adsorption of HCl was equivalent to the oxygen taken up (Table III). They have an entirely different explanation for the adsorption of acids, bases and salts.[11] Their theory is essentially that activated charcoal in the presence of hydrogen or oxygen functions as a gas electrode. In the presence of oxygen, hydroxyl ions appear in solution and the positive charge on the charcoal then attracts anions and adsorbs acids but not alkali. Neutral salts are hydrolytically ad-

TABLE III

Milliequivalents of Oxygen per g. Charcoal	Milliequivalents HCl Adsorbed per g Charcoal
0.012	0.012
0.033	0.035
0.044	0.043
0.052	0.051

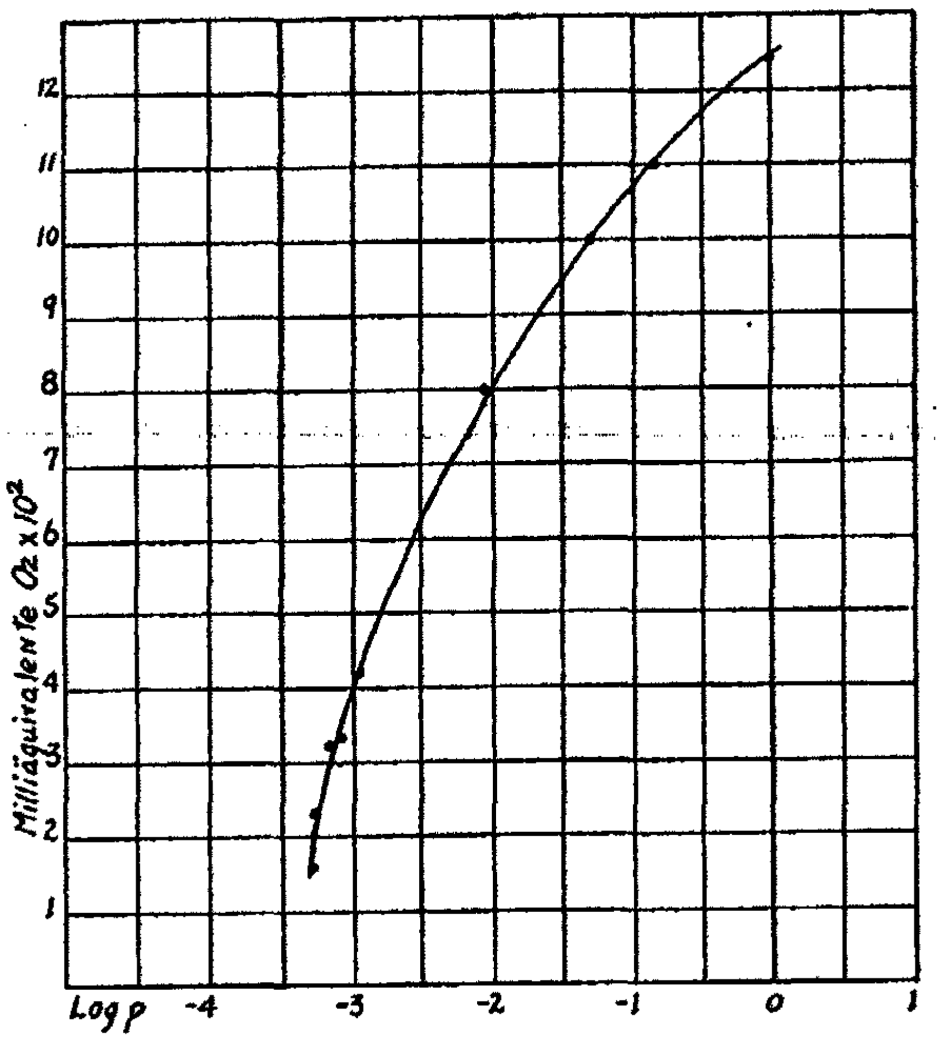


FIG. 4
Frumkin's Curve for Adsorption of Oxygen at Different Pressures

sorbed with the liberation of alkali. In an atmosphere of hydrogen, hydrogen ions appear in solution, leaving the charcoal negatively charged and in a position to attract cations. Alkali is adsorbed but not acid. Neutral salts are hydrolytically adsorbed with the liberation of acid.

Frumkin's early experiments[11] with charcoal alone did not entirely support his theory, but when platinum was incorporated with the charcoal the adsorption of HCl and NaOH in atmospheres of hydrogen and air was in keeping with the theory (Table IV). HCl was adsorbed in the presence of air but not in hydrogen, while NaOH was not adsorbed in air but was adsorbed in hydrogen. Through improvement in technique, however, Frumkin[12] was able to show (Table V) that charcoal even in the absence of platinum behaved in keeping with the theory, and that from potassium chloride in an atmosphere of hydrogen KOH was hydrolytically adsorbed, while in air HCl was taken up. Hydrochloric acid was not adsorbed in hydrogen but was adsorbed in air.

TABLE IV

Per cent Pt.	Milliequivalents HCl adsorbed in Presence of Air	Milliequivalents HCl adsorbed in Presence of Hydrogen	Milliequivalents NaOH adsorbed in Presence of Air	Milliequivalents NaOH adsorbed in Presence of Hydrogen
0.00	0.227	0.190	0.000	0.000
0.004	0.298	0.116	0.000	0.000
0.032	0.333	0.048	0.000	0.426
0.16	0.358	0.000	0.000	0.521
0.80	0.376	0.000	0.000	0.557
4.00	0.393	0.000	0.000	0.576
10.00	0.406	0.000	0.000	0.582

TABLE V

	Charcoal saturated with H_2 adsorbs KOH	Charcoal saturated with Air adsorbs HCl
	KCl Solution	
I	0.0216	0.025
II	0.021	0.025
III	0.0205	

	Charcoal saturated with H_2 adsorbs HCl	Charcoal in Presence of Air adsorbs HCl
	HCl Solution	
IV	0.0	0.14
V	0.0	0.139
VI	0.0	

	Charcoal saturated with H_2 adsorbs KOH	Charcoal in presence of Air adsorbs KOH
	KOH Solution	
VII	0.66	0.0
VIII	0.0655	0.0

TABLE VI

Amount of HCl adsorbed Millimoles		Amount of NaOH adsorbed	
In vacuo	After contact of Charcoal with air	In vacuo	After contact of Charcoal with air
0	0.140	0	0
0	0.140	0	0

Potassium hydroxide was adsorbed in hydrogen but not in air. Frumkin[13] was finally able to demonstrate (Table VI) that in a vacuum, in the absence of both hydrogen and oxygen, neither acid nor alkali was adsorbed. Schilow,[14] however, always maintained that even in vacuo the charcoal adsorbed hydrochloric acid through the agency of his oxide A which was stable even at low pressures and high temperatures, and that KCl was not hydrolytically adsorbed by this oxide. Frumkin[15] questioned Schilow's results and pointed out that it is necessary to continue the heating of the charcoal for twenty-four hours in a high vacuum in order to get rid of all the oxygen. But at the same time with improved technique Frumkin found that the hydrogen atmosphere no longer prevented the adsorption of hydrochloric acid when the concentration of the acid solution was above 0.1 Normal. In concentrations above tenth-normal the adsorption increased rapidly in spite of the presence of hydrogen. This Frumkin attributed to molecular adsorption.

Recently Bretschneider,[16] working in Ruff's laboratory, has reported that the adsorption of succinic acid in air and in vacuo is the same (Table VI). This substantiates Frumkin's findings[11] that the adsorption of benzoic acid is not influenced by the presence of hydrogen or oxygen, even by platinized charcoal. Contrary to Frumkin, Bretschneider found that hydrochloric acid is quite appreciably adsorbed by charcoal in vacuo but in the presence of air the adsorption is increased, practically to the same value for the original charcoal in air. From Bretschneider's curves (Fig. 5) it is apparent that the original charcoal and the evacuated charcoal to which air had afterward been admitted had identical adsorption capacities. The practically constant difference between the values for evacuated charcoal and charcoal in air Bretschneider attributed to the presence of Schilow's oxide B which can bind hydrochloric but not succinic acid. He favors Schilow's theory and states that Frumkin's theory does not afford any better explanation.

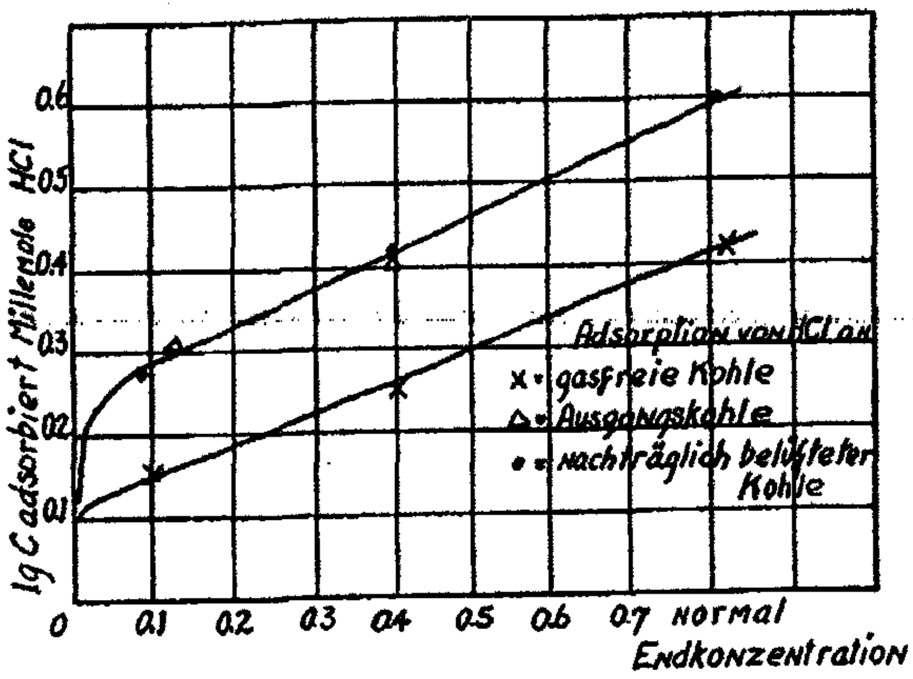


Fig. 5

Bretschneider's Curves for Adsorption of HCl

Discussion

In view of the uncertain and controversial status of much of the evidence for the oxide and gas electrode theories it is difficult, if not impossible, to evaluate them at present. One thing, however, appears to be certain, and that is the section of the field of adsorption of electrolytes from solution to which they apply is very limited. Frumkin and Schilow have both recognized this fact and emphasize that molecular adsorption is not excluded by their theories.

It should be pointed out that, on the whole, the experimental evidence indicates that only those substances which are least adsorbed or not adsorbed at all in the presence of air are influenced by the nature of the gas adsorbed on the charcoal, and these only in lower concentrations. The adsorption of HCl from dilute solutions by charcoal apparently can, under certain conditions, be influenced by the presence of hydrogen, but in higher concentrations it is not affected. Only the first two or three members of the aliphatic acids,[17] which are relatively slightly adsorbed, are appreciably influenced, but the effect falls off rapidly with increase in length of carbon chain. The more strongly adsorbed organic acids such as benzoic and succinic are not affected by the adsorbed gas. The reason for this, Frumkin[11] states, is that acids such as benzoic are like non-electrolytes in their adsorption by charcoal. This explanation encounters serious difficulties when the adsorption behavior of bases is considered.

It is difficult to explain, by either of the theories, why sodium and potassium hydroxides are not adsorbed in the presence of air, while the equally strongly dissociated organic base, tetraethylammonium hydroxide is adsorbed; and again, on the other hand, the weak base, ammonium hydroxide, is not adsorbed. Equally difficult to understand is the fact that the adsorption of KCl, which is exclusively hydrolytic, can be affected by the gaseous atmosphere, while the greater hydrolytic adsorption of potassium benzoate is not affected. Under the circumstances it would be necessary to account for hydrolytic adsorption of potassium chloride by one theory, and hydrolytic adsorption of potassium benzoate by another. The effect of introduction of polar groups on adsorption does not seem to be explainable by either of the theories, nor is the negative adsorption of sodium and potassium hydroxides and its decrease with length of time of contact of charcoal with solution.

Roychoudhury and Mukherjee[18] have put forth the argument against the gas electrode theory that Kruyt's charcoal in oxygen is negatively charged whereas charcoal in oxygen according to Frumkin's theory should be positively charged. If, however, Kruyt's charcoal does contain carbon acids with the carboxyl groups extending into the water phase, the negative charge could arise from the dissociation of the COOH group. This is in keeping with the fact that this charcoal is easily wetted by water whereas the same charcoal heated to a high temperature is very difficult to wet. This charcoal after destruction of the carboxyl groups could, in oxygen, be positively charged according to Frumkin's scheme. It is clearly possible to have charcoal either positively or negatively charged in oxygen, depending upon the conditions of the previous heat treatment, and the argument, therefore, is not a valid one against the gas electrode theory. Furthermore, it seems possible that some of the experimental evidence and procedure employed by Roychoudhury[19] are open to question. In the first place his charcoal was heated at 600° which is not high enough to destroy or drive off the acid products on the surface of the charcoal and they probably are even slowly formed at that temperature, for the optimum is in the neighborhood of 400°. As is evident from the data presented in this and previous papers it is necessary to heat the charcoal around 1000° or above to free it from its acidic properties and to obtain a charcoal that does not take up alkali. Roychoudhury's charcoal, therefore, probably carried some acid products.

Another procedure which is open to question and which may have vitiated some of Roychoudhury's results is that of washing the charcoal with conductivity water to effect purification. In the early work with ash-free charcoal it was repeatedly pointed out[1,20,21] that it is practically impossible to wash out easily measurable amounts of acid by repeated extraction with conductivity water alone. In Table VII are given the results of one experiment which illustrates this fact fairly well. Methods for the quantitative estimation of adsorbed acids on charcoal were developed,[3] and procedures for detecting and measuring acidic and alkaline impurities were devised.[21] In view of the results obtained with these methods it is exceedingly doubtful whether conductivity measurement as carried out by Roychoudhury is any indication of the quantity of acid adsorbed on the charcoal. How futile such a measurement is

TABLE VII

Removal of Adsorbed HCl from Charcoal by Extraction with Water
Each Extraction with 200 cc. Conductivity H_2O

Extraction No.	Period of Contact	Temp.	Acid Removed Cc. 0.02 N
1	15 hours	Room	0.00
2	1 ”	Boiling	1.50
3	30 minutes	”	0.80
4	60 ”	”	1.00
5	10 ”	”	0.40
6	15 hours	Room	0.00
7	5 minutes	Boiling	0.10
8	1 hour	”	0.20
9	2 ”	”	1.10
10	2 ”	”	0.55
11	2 ”	”	0.40
12	1 ”	”	0.20
13	15 ”	Room	0.00
14	10 minutes	Boiling	0.10
15	1 hour	”	0.15
16	1 ”	”	0.20
17	8 ”	”	0.30
18	1 ”	”	0.20

Total HCl extracted by water............................ 7.20
Extracted by boiling with NaOH 7.09

Acid recovered from charcoal equivalent to................14.29 cc. 0.02 N
Chloride ” ” ” ” ”................14.19 ” ”
Acid originally adsorbed on charcoal..... ....14.34 ” ”

as a means of detecting impurities on the charcoal can be judged from the fact that large quantities of acids can be irreversibly adsorbed on the charcoal, leaving no detectible amount of acid in solution. In fact the charcoal will even adsorb acid from a slightly alkaline solution of KCl,[4] and it requires more than one extraction with a considerable excess of alkali at boiling temperature to extract all the adsorbed acid. From the data in Table VII it is evident that equilibrium at room temperature left no acid in solution. At boiling temperature, however, there was an appreciable quantity in solution. The amount of acid removed with each extraction was dependent, not upon the length of time the charcoal was boiled, but upon the temperature at which it was filtered. In fact it is considerably more efficient to extract the acid by percolating boiling water through the charcoal, thus preventing the establishing of equilibrium. This, however, is not to be recommended as a reliable method for removing adsorbed acids, except possibly for removing the bulk of adsorbed acid from a small amount of charcoal. In the experiment summarized in Table VII, 14.34 cc. of 0.02 N HCl was (at room temperature) irreversibly adsorbed on 2.3 g. of charcoal. This furnishes some idea of the quantity of even a slightly adsorbed acid that can be adsorbed without leaving detectible amounts in solution.

That oxides do exist on the surface of the charcoal seems certain from the well known fact that when oxygen is adsorbed on charcoal it is not recoverable as desorbed oxygen but as CO_2 at lower temperatures and as CO at higher temperatures, and that the heat of adsorption of small amounts of oxygen on charcoal is much higher than that of larger amounts. On the other hand, it is not so easy to determine definitely the form in which these oxides exist on the charcoal. Kruyt's idea of intermediate products of mellitic acid seems plausible, for his charcoal, as pointed out above, does have properties in common with charcoal carrying strongly adsorbed complex organic acids.

The idea of basic oxides of carbon does not seem so easily accepted in any case and it is rather difficult to understand why such a basic oxide as Schilow's B should react with HCl but not with benzoic or succinic acids[16] when the fact is that the latter are much more strongly adsorbed by charcoal than is hydrochloric acid.

Additional evidence of the existence of acid oxides of carbon was discovered in the course of the study in this laboratory of methods for the quantitative removal of adsorbed acids from charcoal. An attempt was made to remove the acids by electrodialysis. The following results were obtained:

1. Charcoal heated at 1075°C. (not electrodialyzed) did not adsorb alkali.
2. Charcoal after electrodialysis did not adsorb alkali.
3. Adsorbed HCl was quantitatively removed by electrodialysis.
4. Charcoal from which adsorbed HCl had been removed by electrodialysis did adsorb alkali.
5. Carbon dioxide appeared in both anode and cathode chambers during electrodialysis.

While it was expected that the adsorbed hydrochloric acid would be removed by electrodialysis it was surprising to find that the charcoal after removal of the acid was still able to take up alkali. This was quite contrary to the behavior of the charcoal after adsorbed hydrochloric acid had been removed by other methods. The appearance of relatively large quantities of CO_2 in both anode and cathode chambers during the process of removal of the acid was unexpected. Further investigation will have to be made to elucidate the factors involved, such as the nature of the electrode and membrane materials, and the voltage applied. It is not easy to explain the fact that the charcoal through adsorption and removal of HCl by electrodialysis should acquire the ability to take up alkali. These and many more perplexing facts must await further work before they can be satisfactorily explained.

Summary and Conclusions

1. A brief survey of recent trends and developments in studies on adsorption of electrolytes by ash-free charcoal has been presented.

2. Data have been presented which indicate that negative adsorption of alkali decreases with length of time the charcoal is in contact with the solution.

3. Data have been presented which show that charcoal must be heated at approximately 1000° or above to produce negative adsorption from solutions of sodium hydroxide.

4. Quantitative data have been presented illustrating the practical impossibility of removing even a feebly adsorbed acid such as hydrochloric from charcoal by repeated extraction with boiling water.

5. Adsorbed hydrochloric acid can be quantitatively removed from charcoal by electrodialysis.

6. No one theory alone seems capable of explaining satisfactorily all the known facts of adsorption of electrolytes by adsorbent charcoal.

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[2] Bartell and Miller: J. Am. Chem. Soc., 44, 1866 (1922).
[3] Miller: J. Am. Chem. Soc., 46, 1150 (1924).
[4] Miller: J. Am. Chem. Soc., 47, 1270 (1925).
[5] Kruyt and de Kadt: Kolloid-Z., 47, 44 (1929).
[6] Kolthoff: Personal Communication.
[7] Dubinin: Z. physik. Chem., 140, 81 (1929).
[8] Schilow, Schatunowskaja and Tschmutow: Z. physik. Chem., 149, 211 (1930).
[9] Schilow, Schatunowskaja and Tschmutow: Z. physik. Chem., 150, 31 (1930).
[10] Frumkin, Burstein and Lewin: Z. physik. Chem., 157, 442 (1931).
[11] Bruns and Frumkin: Z. physik. Chem., 141, 141 (1929).
[12] Burstein and Frumkin: Z. physik. Chem., 141, 158 (1929).
[13] Burstein and Frumkin: Z. physik. Chem., 141, 219 (1929).
[14] Schilow and Tschmutow: Z. physik. Chem., 148, 233 (1930).
[15] Burstein, Frumkin and Lawrowskaja: Z. physik. Chem., 150, 421 (1930).
[16] Bretschneider: Z. physik. Chem., 159, 436 (1932).
[17] Lepin: Z. physik. Chem., 155, 109 (1931).
[18] Roychoudhury and Mukherjee: Z. physik. Chem., 157, 435 (1931).
[19] Roychoudhury: J. Indian Chem. Soc., 8, 433 (1931).
[20] Miller: J. Phys. Chem., 31, 1197 (1927).
[21] Miller: J. Phys. Chem., 30, 1162 (1926).

THE REMOVAL OF SULPHUR COMPOUNDS FROM PETROLEUM DISTILLATES

BY HARRY N. HOLMES, A. L. ELDER, AND NORVIL BEEMAN

Sulphur removal has always been recognized as a problem of great importance in the petroleum industry though it may not be as serious as at one time thought. Consultation of the literature will reveal a wide range of materials which have been used either as chemical reagents or as adsorbents to bring the sulphur content of petroleum distillates within the 0.10% limit of the federal government's specifications. The chief chemical reagents for sulphur removal are: sulphuric acid, chlorine and the hypochlorites, liquid sulphur dioxide, and lead plumbite. The principal adsorbents include: fuller's earth, charcoals and activated carbons, clay, bauxite, alumina, and silica gel. On the whole the adsorbents are also excellent clarifiers and it is probably in this rôle that they find, in general, their greatest usefulness.

Silica Gels

Of all the adsorbents, silica gels properly treated, seem to be the most effective both as desulphurizers and as clarifiers. Their advantages lie in the fact that they do not remove such a high percentage of unsaturates or "anti-knock" material as does sulphuric acid.

On page 366 of the Handbook of Petroleum[1] there is shown the following graph, Fig. 1, to illustrate the effect of sulphuric acid treatment upon a distillate containing about 0.87% sulphur. One curve shows the effect of different concentrations of sulphuric acid in pounds per barrel in lowering the sulphur content, while the other shows the loss in volume (largely unsaturates) which accompanies this treatment. Thus with 20 lbs. per bbl., for example, the sulphur was reduced from 0.87% to 0.33%, but this treatment caused a volume shrinkage of 8% to 9%; with 30 lbs. per bbl., the sulphur was reduced to 0.25% but with a 14% loss; with 40 lbs. per bbl., sulphur was reduced to 0.19% with a 20% loss. Heavy sulphuric acid treatment causes not only volume loss but lowers the anti-knock quality as well.

The same handbook gives on page 367 an estimate of the loss of anti-knock materials which accompanies the loss of unsaturates:

8 lbs.	H_2SO_4 decreases the anti-knock value	4.2%
20 lbs.	" " " " " "	10.6%
30 lbs.	" " " " " "	21.2%
40 lbs.	" " " " " "	25.5%

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[1] Handbook of Petroleum, Asphalt and Natural Gas. Bulletin No. 25, Kansas City Testing Laboratory.

Experimental work with silica gel as a desulphurizer has been reported upon by Youtz and Perkins,[1] Borgstrom, Bost and McIntire,[2] Waterman[3] (who in two treatments with 54% silica gel decreased the sulphur content of a Persian oil 20%), Challenger[4] (who calls attention to the fact that silica gel removes only some sulphur compounds from mineral oils), Holleman,[5] Koetschau[6] (with a review of the literature), Miller[7,8] (with description of an oil refining plant using powdered silica gel), Waterman and Perquin,[9] Waterman and Tussenbroek,[10] Wood[11,12] (who studied the removal of sulphur and sulphur compounds from naphtha and found silica gel better than fuller's earth and alumina), Gladys E. Woodward[13] (who found that from a naphtha solution a commercial gel removed 18% and a Holmes' gel 37% of the sulphur), and Bosshard and Wildi[14] (who suggest that in treating lubricating oils the coloring matter may be removed by a preliminary treatment with gels having coarse pores followed by gels with finer pores for sulphur removal).

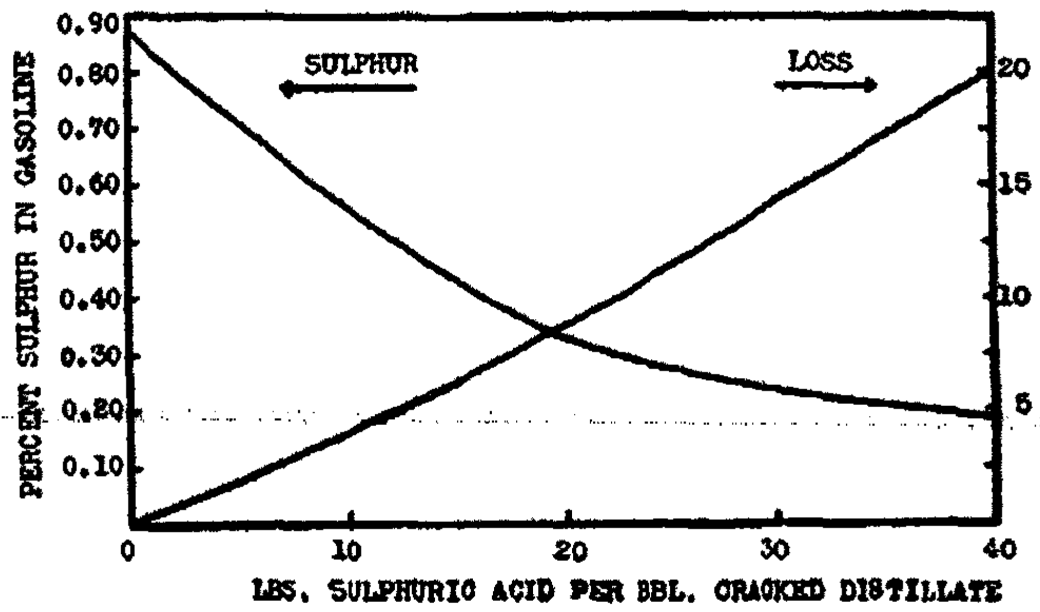

FIG. 1

The Sulphide-Coated Gels

Although ordinary silica gel, activated but otherwise untreated, is a good remover of sulphur compounds from petroleum oils, the senior author early planned to use silica gel coated with metallic sulphides.

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[1] Ind. Eng. Chem., **19**, 1247 (1927).

[2] Ind. Eng. Chem., **22**, 87 (1930).

[3] J. Inst. Petr. Tech., **11**, 576 (1925).

[4] Ind. Chem., **2**, 445 (1926).

[5] Chem. Weekblad, **21**, 187 (1924).

[6] Chem.-Ztg., **48**, 497 and 518 (1924).

[7] Oil and Gas J., **23**, 104, 151, 158 (1924).

[8] Trans. Am. Inst. Chem. Eng., **15**, 241 (1923).

[9] Brennstoff Chem., **6**, 255 (1925).

[10] Brennstoff Chem., **9**, 397 (1928).

[11] Oil and Gas J., p. 146, Feb. 24, 1927.

[12] Ind. Eng. Chem., **18**, 169 (1926).

[13] Ind. Eng. Chem., **21**, 693 (1929).

[14] Helv. Chim. Acta, **13**, 572 (1930).

It might be thought that PbS, CuS, etc., freshly prepared and activated could serve alone without the support of a gel structure. This was tried in the Johns Hopkins Laboratory[1] and it was found that "ethyl mercaptan was readily removed when shaken with amorphous cupric, lead, stannic, cadmium and arsenious sulphides. Cupric sulphide was immediately affective as an adsorbent for the removal of secondary amyl mercaptan." It would have been more interesting if this work had been done on an actual petroleum distillate from which the sulphur compounds are almost always less readily removed than a comparatively simple mercaptan. One of us (A.L.E.) working with a cracked California distillate was able to get only a negligible sulphur removal with precipitated and activated CuS. The conclusion reached was that CuS without the support of the gel did not offer a sufficiently large area of active surface for the appreciable removal of sulphur compounds commonly found in cracked petroleum distillates.

The Silica Gel Support

The gel used as a support for the sulphide coating was that known colloquially in this laboratory as "white gel" or "gel from iron." Instead of precipitating the silicic acid gel from water glass by the addition of HCl,[*] gel is prepared by stirring together intimately dilute solutions of $FeCl_3$ and sodium silicate in such proportions as to give a mixture neutral to litmus.[2,3] Time is given for the gel to set and drain. It is then broken into lumps and allowed to dry to about 45% water content when it is bottled to synerize for a few days. The "red gel" resulting, actually a molecular mixture of the hydrated oxides of iron and silicon, may itself be activated and used as an adsorbent.

However, the support we employed for sulphides was not the "red gel" but the "white gel." To obtain the "white gel" from the chocolate-brown material, the "wet-heat treatment" is given with hot 9N H_2SO_4. This removes the ferric oxide leaving when dried at 150° to 200° a white porous product of slightly hydrated silica.

This particular "wet-heat treatment" produces a gel of the "medium vitreous" type and which was found by Ross[4] to be, when coated with CuS, the most efficient sulphur remover of all the similarly coated gels with which he worked. In contrast to this it might be pointed out that Holmes and Elder[5] found that the benzene-adsorption capacity of the Holmes' "chalky gel" was far greater than the vitreous and glassy type. As has been pointed out, the "wet-heat treatment" provides an excellent means of securing any desired capillary size from the "vitreous" which has the appearance of broken china with capillaries averaging 8 to 10 $m\mu$ in diameter, to the "chalky," which possess a soft, easily powdered structure with capillaries from 10 to 20 $m\mu$. The

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[*] U. S. Pat. 1,297,724 by Silica Gel Corporation.

[1] Ind. Eng. Chem., 21, 1033 (1929).

[2] Ind. Eng. Chem., 17, 280 (1925).

[3] Ind. Eng. Chem., 18, 386 (1926).

[4] Master's Thesis, Oberlin College, May (1931).

[5] J. Phys. Chem., 35, 82 (1931).

commercial gel of the Silica Gel Corporation is of the hard, glassy type with capillaries approximately 4 to 5 mμ in diameter.

In general the higher the water content before the "wet-heat treatment" and the higher the temperature of the water or the acid of the "wet-heat treatment," the larger the capillaries.

The Sulphide Coating

Various methods of securing uniform deposits of finely divided metals, metallic oxides and sulphides throughout porous solids have been investigated in this laboratory.[1] The best CuS coating is secured by soaking the "white gel," obtained by a 45%–60° "wet-heat treatment," in a solution of $CuSO_4$, draining off the excess $CuSO_4$, drying for about two hours in nitrogen or CO_2, cooling to 0° and saturating with H_2S gas, washing and drying up to 200° in in an inert gas such as nitrogen or CO_2. Free sulphur is always formed in the gel in this process and it must be removed before the gel can be used as a desulphurizer.

The possible source of the sulphur found in the CuS coated gel at this stage in its preparation may be H_2S or CuS both. The H_2S may be cracked on the gel surface, or it may be so strongly adsorbed by the CuS coating that even repeated washing does not remove it. In the latter event, it is left to be cracked later when the gel is heated for activation.

That it is possible for H_2S to be strongly adsorbed by CuS was pointed out in 1892 by Linder and Picton[2] and more recently by Kolthoff.[3] There is little reason to suppose that CuS should hold H_2S more strongly than other sulphides, PbS and CdS, for example. As a matter of fact PbS coated gel and CdS coated gel may both be washed until free from sulphide ions. When heated in nitrogen neither washed product gave the slightest evidence of free sulphur. We are forced to turn then to the other possible source, the CuS itself.

It is well known that CuS breaks down at red heat in the absence of air into Cu_2S and free S, and that the Cu_2S is stable over a wide range of temperature. This decomposition probably occurs to a limited extent at lower temperatures. When the gels were heated in exactly the same manner the CuS gave a sulphur deposit upon the tube walls while the PbS and CdS coated gels did not.

Activation and Use of Adsorbents

When the CuS coated gel is heated any free sulphur formed is driven off and activation is accomplished by the same process and at the same time. As might be expected the time period and the temperature at which the activation is carried out has a profound influence upon the efficiency of the gel as an agent for removing sulphur compounds from petroleum oils.

In the investigation of activation temperatures a series of experiments was run with different types of gels, 10–20 mesh, on an untreated California

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[1] Colloid Symposium Monograph, **6**, 283 (1928).

[2] J. Chem. Soc., **61**, 120 (1892).

[3] J. Phys. Chem., **36**, 861 (1932).

cracked distillate* containing 0.363% sulphur. The procedure with each gel was to shake 3 volumes of the gel with 5 volumes of the distillate for 1/2 hour, decant off the oil, centrifuge it, filter, and analyze by the sulphur lamp. The main purpose of these experiments was to determine the activation temperature with each gel which gave the maximum sulphur removal. It would probably be unwise to draw conclusions from this series as to the relative superiority of one type of gel over another, because the original gels from which these were prepared differed one from the other in water content and other respects. It would have been interesting, for the sake of comparison, had the gels all come from a common source, but this was not so and the reader must be warned against drawing unwarranted conclusions.

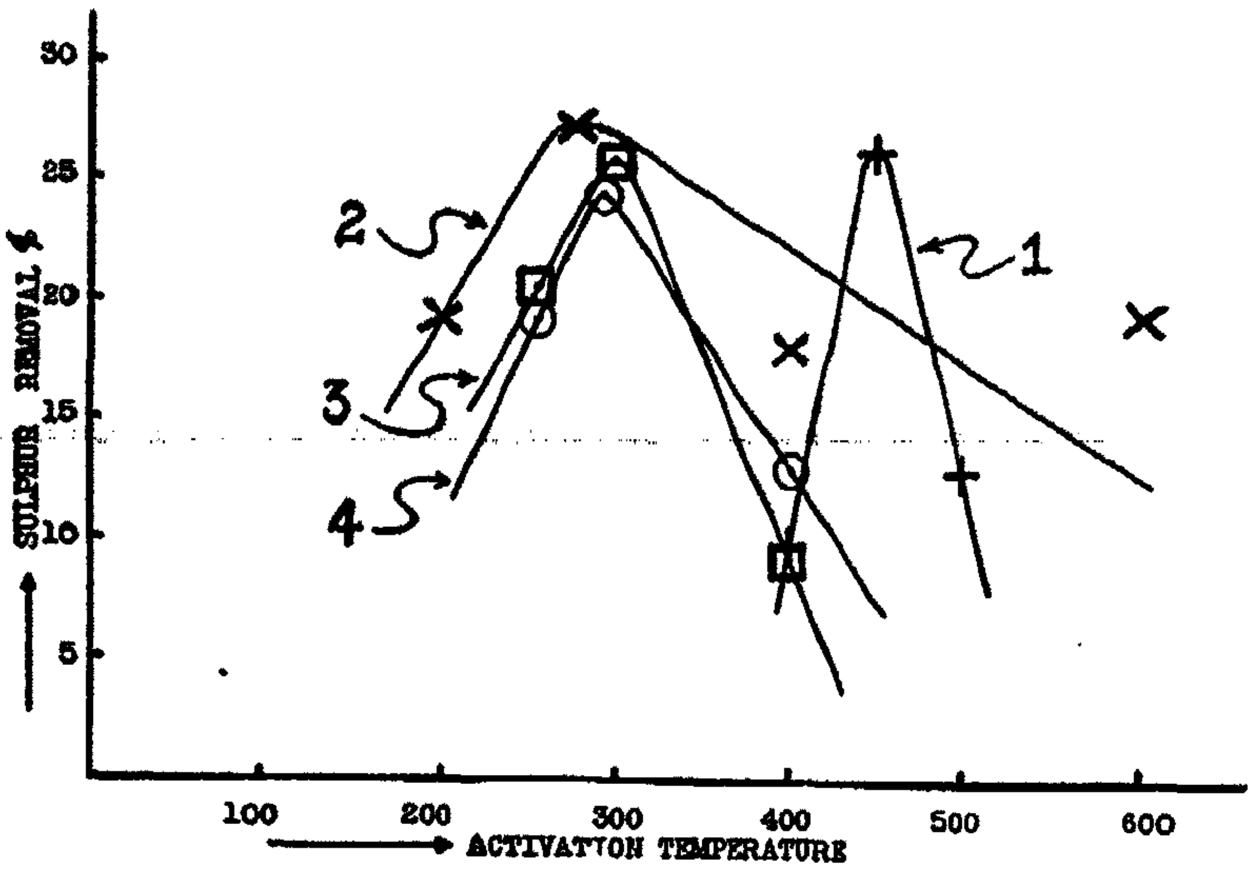

FIG. 2

Effect of Activation Temperature upon Sulphur Removal.
Curve 1: CuS coated gel, activated in nitrogen.
Curve 2: "Red gel" activated in air.
Curve 3: "Red gel" kerosene treated, activated in nitrogen.
Curve 4: "Red gel," kerosene treated, activated in air.

Curve 1 of Fig. 2 is that of a CuS coated "white gel" which had been given a "wet-heat treatment" of 42.2%-60°. The gel was activated two hours with slowly rising temperature in an electric tube furnace in a stream of nitrogen. For each activation the gel was placed in the furnace at room temperature, the air swept out by nitrogen, and the electric current turned on. The temperature was measured with a thermocouple. It is observed that the maximum on the curve falls on the 450° ordinate with a removal of 26.6% sulphur. To the left of the maximum the curve in reality drops below the horizontal axis (not shown in the figure) because at these lower temperatures the sulphur formed by the decomposition of the sulphide is not all driven off, with the consequence that

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* The California distillates used in this work were furnished through the courtesy of the Universal Oil Products Company, Chicago, Illinois.

the distillate actually dissolves the sulphur during treatment, and, instead of removal, there is an actual increase in sulphur content of the oil. To the right of the maximum the curve again falls off rapidly but never to a zero removal. This drop to the right may be explained in part by the change of the CuS to Cu_2S. Each point through which the curves are drawn is an average of two or more determinations and in some instances a half dozen or more. The general shape of the curve was confirmed by subsequent work and there can be little question about the location of the maximum.

A study of this curve and a consideration of the facts brought out in connection with the discussion of the presence of free sulphur in the gel, suggested that a vacuum activation at lower temperatures would prevent to some extent the decomposition of the CuS and at the same time make removal of the sulphur possible at lower pressures and lower temperatures. This was done and the best and most consistently high removals of sulphur from gasoline were obtained by CuS-coated gels activated in this manner. The gels were heated in nitrogen at a pressure of 2.0–2.5 cm at temperatures ranging from less than 200° to about 300°C. Over the range between 225° and 270° the best results were obtained. Gels treated in this manner removed more than 30% of the sulphur.

The other curves in Fig. 2 have to do with the same distillate but treated with different "red gels," though the proportions, time of treatment, etc., were in general the same as with the CuS-coated gel. Curve 2 is that of a "red gel" activated in air. With this gel the maximum sulphur removal occurs with an activation temperature of about 275°C at which 27.6% of the sulphur was removed from the distillate.

Curve 3 is for another "red gel" but with the difference that it was dried below 200° before activation, soaked in kerosene for a day, drained, and then activated in a slow current of nitrogen. Here the maximum is the average removal of 26.2% and falls on the 300° ordinate. Similarly Curve 4 is for a "red gel" kerosene-treated but activated in a current of air. The maximum represents a removal of 24.8% when the gel was activated at 290°C.

Duplication of these curves is not difficult when the preparation of the gels is carefully controlled, that is, when the water content of the original gels is always the same before "wet-heat treatment," and the activation carried out each time in exactly the same way.

The Sulphur Lamp

The sulphur analyses were made with the A.S.T.M. lamp. From time to time in recent years several changes have been proposed in this lamp for the purpose of increasing the accuracy and of making it more generally useful in the analysis of various grades of oil. Some of these more recent suggestions have come from: Wood and Mattox[1] with a cooling device for regulating the flow of oil, thus rendering it more satisfactory for both heavy and light oils; Edgar and Calingaert[2] with a metal collar to radiate the heat away from the

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[1] Ind. Eng. Chem. Anal. Ed., 2, 24 (1930).

[2] Ind. Eng. Chem. Anal. Ed., 2, 104 (1930).

flame and a porous fritted glass disc in place of the beads in the adsorption tube; from Luis Bermejoy Vida[1] making use of a long quartz combustion tube in which the sample is placed after being soaked up in absorbent cotton and said to give results equal to or a little higher than the bomb; and Formanek[2] with an improvement on the apparatus of Engler-Heusler permitting a larger flame, faster burning of the oil, and better absorption of the sulphur oxides.

The form used in this laboratory during 1931–32 is shown in Fig. 3. The essential difference from other forms lies in the sliding glass collar which makes possible a quick adjustment of the flame. This glass collar is held in place by the radiator of sheet brass which in turn is held by two spring clamps to the wick tube of the lamp. At first, our method of analyzing heavy oils was the somewhat doubtful one of diluting with a good grade of gasoline before placing it in the lamp, but later the lamps were fitted with a small "pilot flame" which burned sulphur-free alcohol. A small test tube holding the alcohol, stoppered with a slotted cork carrying a long wick tube was clamped in such a way as to bring a small alcohol flame to the wick of the sulphur lamp. This auxiliary flame served to steady the burning by warming the heavy oil just at the proper place and by reducing appreciably the formation of tarry crusts over the end of the wick.

Some idea of the accuracy obtained by the lamp may be given by saying that in ordinary routine analyses of gasolines the variation of any one determination from the average of a triplicate run did not exceed 4% of the total sulphur except when unusual difficulties were experienced, such as excessive gumming or encrusting of the wick. The amount of oil burned for each determination was approximately one gram, determined by taking the difference in weight of the lamp before and after burning.

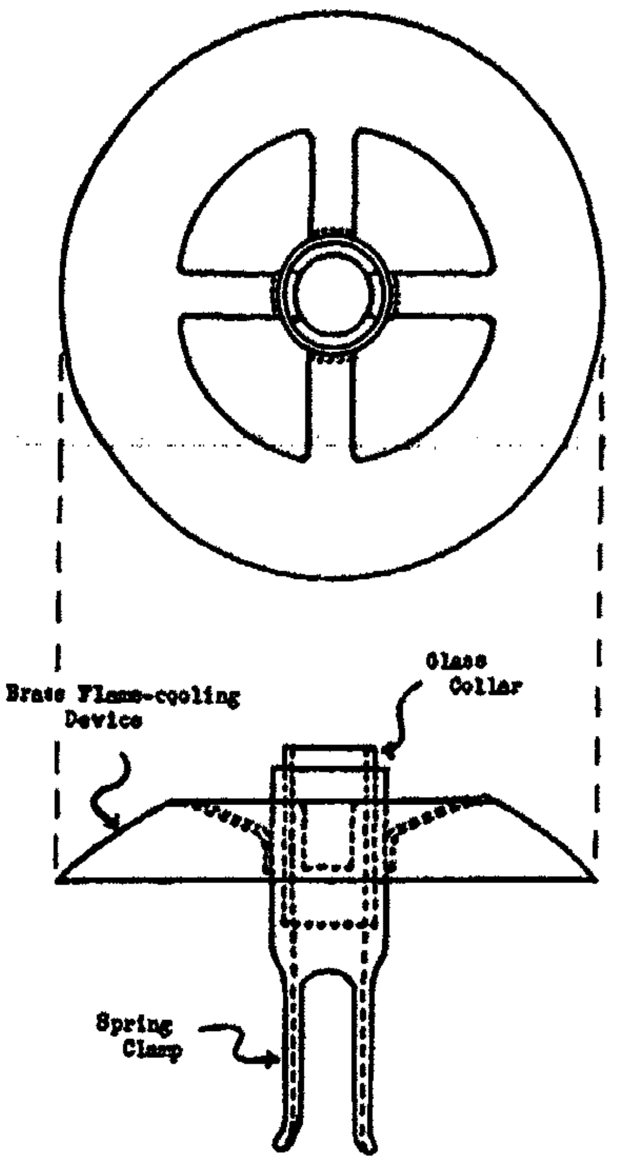

Fig. 3
Sections of Flame-cooling Device for the Sulphur Lamp

It was thought that some of the inaccuracy of the lamp might be due to the fact that not all sulphur was burned to SO_3. If burned only to SO_2 instead of SO_3 more acid would be required in titration and this would give an apparently lower sulphur content in analysis. In order to get some evidence at this point an investigation was made of the amount of SO_2 converted into SO_3 during the burning in the lamp of a solution of SO_2 in a sulphur-free alcohol. The SO_2 was

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[1] Chimie et Industrie, Special No., 189-95, March, 1930.

[2] Chem. Obzor, 6, 36 (1931).

taken from a small lecture table cylinder of the gas. After the burning the sulphites which were formed by reaction between the SO_2 and Na_2CO_3 were determined by iodine titration. If only SO_3 and no SO_2 had passed over into the $NaCO_3$ we would have:

In the absorption tube:

(a) $SO_3 + H_2O + Na_2CO_3 \text{ (excess)} \rightleftharpoons Na_2CO_3 \text{ (remaining)}^{*} + Na_2SO_4 + H_2CO_3.$

In the titration with acid using methyl orange:

(b) $Na_2CO_3 \text{ (remaining)}^{*} + 2\,HCl \rightleftharpoons 2NaCl + H_2CO_3.$

If only SO_2 and no SO_3 we would have, on the other hand:

In the adsorption tube:

(c) $SO_2 + H_2O + Na_2CO_3 \text{ (excess)} \rightleftharpoons Na_2CO_3 \text{ (remaining)}^{*} + Na_2SO_3 + H_2CO_3$

In the titration:

(d) same as (b)

(e) $Na_2SO_3 + HCl \rightleftharpoons NaCl + NaHSO_3$ and then a slight excess of acid would give the end point with the indicator.

Now it was found by analysis of the solution in the absorption tube that about 90% of the SO_2 had been converted into SO_3 leaving 10% unchanged. An examination of the equations involved makes it plain that except for equation (e) the amount of acid required in a titration would be the same whether the gas were SO_2 or SO_3. But if 10% is SO_2, since in accordance with equation (e) the sodium sulphite would act with methyl orange as a mono-acid base, 5% more acid would be required to give the end point and the analyst would report 95% of the sulphur present.

It is interesting to note that Wood and Mattox with their modified lamp accounted for 92% to 95% of the sulphur (as carbon disulphide) present in gasoline and kerosene, and that Edgar and Calingaert accounted for 95.7% in pure heptane.

Results with Sulphide-Coated Gels

1. *Sulphur from Gasoline.* One of us (A.L.E.) working with a gasoline which contained 0.597% sulphur, treated it with several different sulphide-coated "chalky" gels and obtained the results tabulated below. Three volumes of the gel were shaken for 1 hour at room temperature with 5 volumes of gasoline:

Gel coating	% S after treatment	% S removal
MnS	0.430	12
PbS	0.479	20
FeS	0.447	25
Ag_2S	0.430	28
CuS	0.405	32

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* For the sake of simplicity this is left as Na_2CO_3, but of course it would be largely the bicarbonate formed in the presence of CO_2 during the combustion of the oil.

It is seen from this that CuS-coated gel is more effective as a sulphur remover than any of the others mentioned.

2. *Thiophene from Gasoline.* From a solution of 0.597% thiophene by weight in a very good quality of gasoline 34% was removed by treatment with CuS-coated chalky silica gel at a temperature of −10°C, while PbS-coated gel removed only 24%. When the temperature was lowered still more by cooling with CO_2 snow the removal with CuS gel was 42% and with PbS 32%. (A.L.E.) This increased removal at the lower temperature strongly indicates adsorption as a part of the removal action.

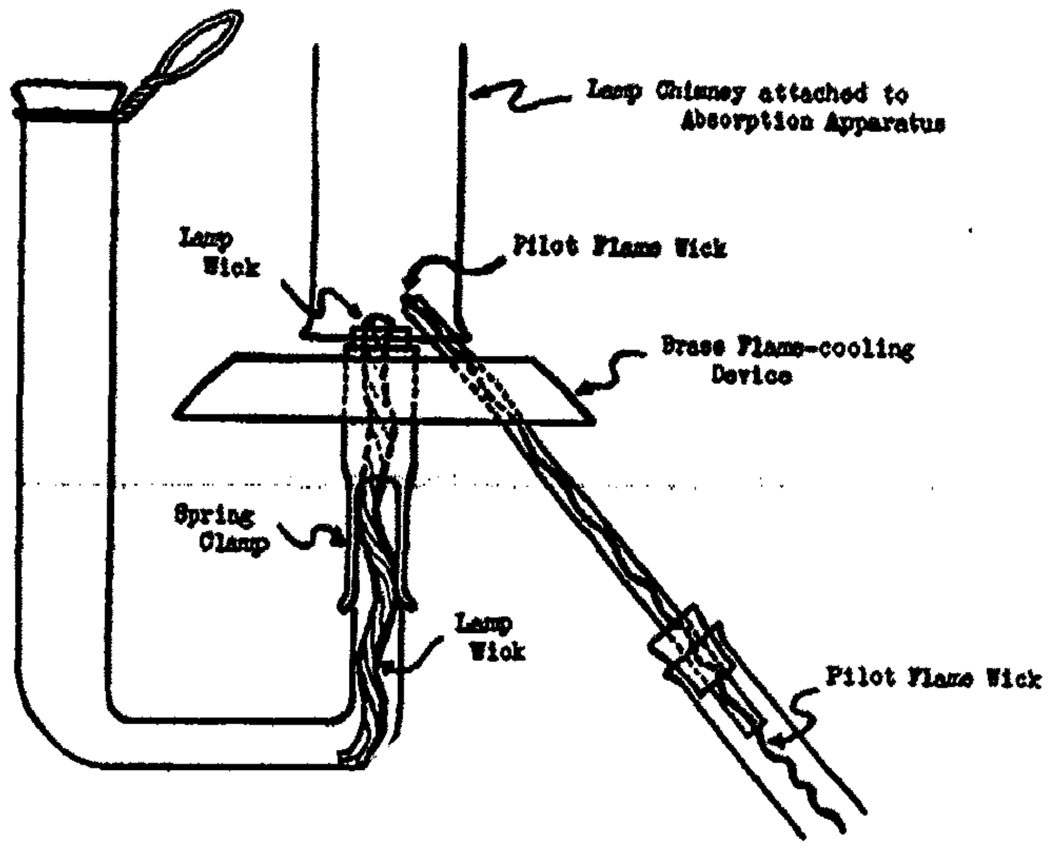

Fig. 4
Sulphur Lamp Assembly for Heavy Oils

It is rather to be expected that removals are generally a combination of adsorption and chemical reaction. For some compounds adsorption predominates.

3. *Sulphur from Shale Oil.* Thick viscous oils have a tendency to cover the outside of the gel particles and thus block the capillaries and prevent free access of the oil to a large part of the active surface of the gel. To meet this problem our shale oil was fractionated and the fractions worked with separately. The lighter the fraction the more easily was the sulphur removed, but even with these lighter fractions gumming of the gel was a source of trouble and the sulphur removals small.

A fraction boiling between 250°C and 300°C was treated for one hour by shaking with CuS-coated gel in the ratio of 3:5, by volume of gel to oil, and the sulphur content was reduced 9.8%. On the other hand, a fraction boiling between 300°C and 350°C showed no removal with the same treatment. But this same fraction after a preliminary treatment with 6 grams anhydrous $AlCl_3$ per 100 cc. oil gave a total removal of 10.3% when followed by treatment with CuS-coated gel.

An entirely different fraction, boiling between 200°C and 250°C, was treated as follows:

Preliminary treatment		Followed by	
Reagent	% removal	Reagent	Total % removal by both
CuS gel	nil	—	—
$AlCl_3$	nil	CuS gel	9.9%
H_2SO_4	1.9%	CuS gel	13.8%
"Red Gel"	0.7%	CuS gel	16.5%

In reviewing all the work with shale oil it can be said that preliminary treatments in general averaged less than 5% removal. These preliminary treatments, however, evidently removed substances which interfered with the effectiveness of the CuS-coated gel, for when followed by a treatment with the gel better removals were obtained than with the gel alone. The above table is presented to show the general tendency discovered, not to claim decimal point accuracy for the results obtained.

Freshly fractionated shale oil was generally light in color but darkened rapidly with age. After a time a gummy sludge invariably settled out.

4. *Use of Regenerated CuS-coated Gels with Gasoline.* A CuS-coated gel, 10-20 mesh, which had previously removed about 25% sulphur from an untreated distillate, was recovered by heating in nitrogen gas at a temperature of 275°C. It was then again used in the treatment of a fresh sample of the same distillate and found to remove 25.4% sulphur. Another CuS-coated gel, powdered to 50 mesh, was recovered in the same manner and found to take 29.9% sulphur from a fresh sample of the distillate.

Regeneration by roasting in the air was also tried, since this, if feasible, would be somewhat cheaper on an industrial scale than regeneration in nitrogen or carbon dioxide. But the roasting would have to be so carried out that the CuS did not oxidize excessively. It was very interesting to discover that the heating of a 10 to 15 gram sample of once-run CuS-coated gel in an open dish until it catches fire and burns off without further external heating makes just about the right combination of length of time and height of temperature. The temperature rises in such a roasting to 380°C or 400°C but that temperature is maintained only for a few minutes. Larger samples would probably heat up more, especially if stirred during the burning off. Some of the once-run CuS-coated gel, 10-20 mesh, mentioned above, was thus heated in an open dish and as soon as the flame had died out and the gel cooled somewhat, was used in the treatment of a fresh sample of distillate with the result that 28.2% of the sulphur was removed. It was similarly reactivated again and upon the third treatment of a fresh sample there was an average removal of 27.3%.

These re-runs with re-generated gels are significant in that they point to the recovery and re-use of the gels a number of times before they become exhausted. Even after use and recovery two times, when the re-generation was by a method calculated to be very severe upon the gel, little deterioration was shown, for on the third run almost as much sulphur was removed as before.

Results with a Silica Gel

The uncoated silica gel, *i.e.*, the "white gel," was found to have a powerful adsorbing action for sulphur compounds in gasoline but on the whole was not as good a sulphur remover as the CuS-coated gel. The vitreous type of silica gel removed sulphur better than the very chalky, but a semi-chalky gel was the best of all.

A "white gel" which had been given a preliminary treatment with kerosene after activation was the most satisfactory of the "white gels" for sulphur removal. (A.L.E.) Thus a gel of the vitreous type was shaken with a distillate containing 0.76% sulphur. The ratio of gel to oil was 3:5 by volume and the period of treatment one hour. The removal obtained was 32%. But when this gel was given a preliminary kerosene treatment the removal was increased to 40%, one of the highest single removals with kerosene-treated silica gel. A sample of Patrick's gel under similar conditions removed 36% and after it had been given the kerosene treatment removed 37%. (A.L.E.) In another treatment of the same distillate with the same ratio of gel to oil, using the Holmes' semi-chalky gel, kerosene treated, the removal was 30%. The more vitreous Patrick's gel, used in the same way including kerosene treatment, removed 20%. It is evident that the semi-chalky gel with the larger pores removes sulphur from gasolines more efficiently. (A.L.E.)

Results with the Red, Hydrated Ferric-Oxide-Silicon-Dioxide Gel

A vitreous type of "red gel" prepared from sodium silicate and ferric chloride in such proportions as to be neutral to litmus, was the type of this gel most favored for sulphur removal. (A.L.E.)

A California distillate containing 0.76% sulphur treated for 1 hour at room temperature with this neutral type of "red gel," in the ratio of 3:7 gave a removal of 14%, while another in the ratio of 3:5 removed 23%. This latter, after a preliminary treatment with kerosene, was much improved and removed 27%. Other "red gels," after receiving the kerosene treatment, removed sulphur from gasoline as follows: one in the ratio of 1:2 after a 4 hour shaking with the sample removed 24%, another in a 2:3 ratio and a 3 hour shaking removed 27%. In all these preliminary treatments of the gel, kerosene proved better than gasoline or any light oil. (A.L.E.)

It was noted that lower fractions of refined and redistilled kerosene did not do as well as the higher in the matter of sulphur removal. This lends support to the idea that oil used for this preliminary treatment must be of sufficiently high boiling point to drive off water adhering to the gel surface. Dunstan, Thole and Remfry[1] have pointed out in connection with their experiments with bauxite that if air is admitted to the freshly activated bauxite it becomes less active. This same thing may be said here in connection with the gels. The oil may not only drive off water but may prevent or delay adsorption of moist air on the gel surface.

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[1] J. Soc. Chem. Ind., **43**, 127 T (1924).

Double Treatments; Combination Treatments

By double treatment is meant the further treatment of the same, already treated distillate by a fresh sample of gel. Double treatments of shale oil have been reported upon in the paragraph on "Sulphur from Shale Oil." Double treatments of gasolines follow here.

One of the best results from double treatment was obtained with a vitreous "white gel" of 20 mesh on a California distillate containing 0.76% sulphur when 50 cc. of the gel were shaken with 100cc. of distillate and then allowed to stand for 12 hours. Upon analysis this treatment was found to remove 24% of the sulphur. A second treatment of this once-treated distillate in exactly the same manner with a fresh sample of gel gave a further removal of 21%, or a total by the combined treatments of 55%. This was repeated and the average of the two sets of double treatments came to 47%. (A.L.E.)

Color Removal

The "red," "white," and CuS-coated gels all remove color very well. The concentration ratio of 3 volumes of gel to 5 volumes of distillate can always be counted upon to remove about 95% of the color by shaking them together for ½ hour.

The best color removal obtained was with a "white" gel which had received a preliminary treatment with oleic acid. This gel in the ratio of 2:5 removed all the color from a California distillate when shaken for 1 hour. (A.L. E.) "Red gel" is also a very effective color remover, both kerosene treated and untreated as 3 volumes of "red gel" shaken 1 hour with 5 volumes of distillate removed 99% of the color. (A.L.E.)

Regenerated gels, both "red" and CuS-coated, were found to remove almost all the color from brownish yellow gasoline. Samples of these gels regenerated in an open dish by heating until they caught fire, when shaken for ½ hour in the ratio of 3:5, removed 99% of the color.

Effect of Aging upon Cracked Distillates

Though this matter has not been investigated thoroughly, it has been observed that the sulphur compounds in cracked distillates undergo change with age. The insides of containers become covered with a thin dark deposit and the sulphur compounds evidently change in composition or polymerize or become altered in such a way as to show a lower sulphur content upon analysis with the sulphur lamp. Variation in results obtained over a period of months or years through the use of gels prepared in much the same way is explained by this aging of the distillates and change in the sulphur compounds with consequent change in the ease with which the sulphur compounds can be removed.

Summary and Conclusions

1. It has been shown that cupric sulphide is superior to other metallic sulphides in removing sulphur compounds from petroleum distillates.

2. Silica gels, thoroughly impregnated with cupric sulphide, are superior to metallic sulphides without the gel support.

3. The efficiency of the sulphide-coated gels varies greatly with the activation temperature.

4. During activation of the cupric sulphide—silica gel free sulphur is released, in the formation of cuprous sulphide, and must be driven out by adequate heating.

5. The gels described may be regenerated and used repeatedly with good results.

6. Adsorption methods of sulphur removal do not, like the sulphuric acid treatment, cause a heavy loss of valuable anti-knock fuel.

7. An improved form of sulphur lamp for the oil industry is described.

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THE STUDY OF GELS BY PHYSICAL METHODS

BY EMIL HATSCHEK

The present paper is in the main a record of experimental investigations which do not claim to be more than the first steps in two distinct lines of inquiry. It seemed to me first of all desirable to gain some insight into the elastic properties of a number of gels other than gelatin, which so far has almost exclusively received the attention of investigators and, with the exception of the benzyl alcohol gel of cellulose acetate, is the only one for which Young's modulus has been determined for a range of concentrations. A knowledge of this constant appears to be indispensable for forming any idea of the structure of a given gel, and I have accordingly determined by a method not hitherto employed the modulus of agar gel, silicic acid gel and formaldehyde-gelatin gel, as well as followed its variation with age.

In the second place it seemed advisable to study the effect of deformation on various physical properties of one gel more exhaustively than has been done so far, and to discriminate between the changes brought about by reversible and irreversible deformation. Gelatin is most convenient for this purpose. The investigation, so far as it has been carried, covers the changes produced by both types of deformation in (a) accidental birefringence, (b) tensile strength and (c) permeability to a solute, *i.e.*, diffusion velocity in the gel.

Finally some of the theoretical implications of the experimental findings are discussed very briefly.

The first physical constant of gelatin gels to be measured was Young's modulus. The earlier investigations by Maurer, Bjerken, Fraas and Leick[1] may be assumed to be generally known. They were undertaken with a view to studying the elastic behaviour of a material in which small stresses produced considerable deformations and optical anisotropy which could be readily observed, while it exhibited in addition interesting anomalies; a combination of features which have no doubt secured for the results inclusion in the hand-books of physics, like Winkelmann's. The intensive study which gelatin sols and gels have received within the past two decades has produced further determinations of Young's modulus, carried out with somewhat different intentions, such as testing the validity of mathematical deductions from assumed structures, among which must be specially mentioned those by Sheppard and his collaborators[2] and by Poole.[3]

It is a striking illustration of the strength of tradition or of habit that, with the exception of Sheppard's, all measurements have been made on test pieces in tension. This is the obvious method for *e.g.*, metals, but in adapting

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[1] Maurer: Wied. Ann., 28, 628 (1886); Bjerken: 43, 917 (1891); Fraas: 53, 1074 (1894); Leick: Drude's Ann., 14, 139 (1904).

[2] J. Am. Chem. Soc., 43, 539 (1921).

[3] Trans. Faraday Soc., 21, 114 (1925).

it to gel specimens the earlier workers found some difficulty in clamping the ends. This difficulty is now avoided by Sheppard's method of attaching the ends of the specimens to wood blocks—a method used successfully by Poole on gels of as low concentration as 3.23%, which could not conceivably have been handled in tension by any other method—the application of which is, however, obviously confined to gels which adhere to wood. The only one of this kind which has so far been investigated, also by Poole,[4] is the benzyl alcohol gel of cellulose acetate, which in its general elastic behaviour closely resembles gelatin gel.

It is difficult to see why apparently no attempts have so far been made to determine Young's modulus by compression. The method has obvious advantages even for adhesive gels, and is applicable to gels which cannot be attached to supports or clamped, such as agar and silicic acid gels. Although a re-determination of the modulus of gelatin gels is not one of the main objects of the work to be described in the present paper, a good deal of it is concerned with the changes produced in various properties of gelatin gels by compression and the method was therefore first tested on such gels.

The test pieces were cylinders, mostly 31.5 mm in diameter, with plane ends, the length not exceeding 1.4 diameters. If the test piece is to keep—very approximately—cylindrical under pressure, the plane ends must slide freely over the surfaces between which they are compressed. It is difficult—at any rate I have found it so—to cut gelatin cylinders, expecially at the lower concentrations examined, so that the resulting surface will be really plane and will slide freely even over oiled metal surfaces. It therefore appeared desirable, and was in any case necessary for the diffusion experiments to be described later on, to produce the two plane end faces directly on the castings. There is of course no difficulty in obtaining one plane end, by using a cylindrical mould closed at one end by a plate of some material to which gelatin does not adhere, but the free surface on cooling sets to a concave meniscus, even if the mould consists of a material to which gelatin does not adhere. The procedure finally adopted for all cylindrical gelatin specimens was as follows: the moulds were lengths of brass tubing cut off in the lathe. One end was closed by a shallow flat metal dish in which sufficient paraffin wax had been melted to form a layer about 2 mm deep. The previously warm lengths of tube were placed in the dishes which stood on a levelled table and were allowed to cool on it. The moulds were carefully greased with vaseline and filled with the gelatin sol at a temperature of 35 to 40°. To avoid meniscus formation sufficient liquid paraffin, a few degrees warmer than the sol, to form a layer 2 or 3 mm deep is poured on the sol and, like the paraffin wax in the bottom, forms a small concave meniscus with the wall. The gel cylinder is accordingly bounded by two plane ends at right angles to the axis and the two circular edges are rounded off by the menisci. While this makes the pressure distribution a little less regular than it would be in the absence of the rounding off, these test pieces slide more freely than any cut faces which I have ever managed to produce. The mould is illustrated in Fig. 1.

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[4] Trans. Faraday Soc., **22**, 82 (1926).

The determination of the modulus was carried out in the press illustrated in Fig. 2. The top plate A' was gun metal in one case, and aluminium in others, to reduce the minimum load which could be used. It was further loaded by "cheeseweights," *viz.* small tins filled with shot and weighing 200 gm each. The press was mounted with the measuring microscope on a common levelled base plate. The faces A A' were well oiled or vaselined.

The specimens were loaded, first with the top plate alone, and then with successive further loads of 200 gm each and the lengths, either between the ends of the specimens, or between Indian ink marks placed near the ends, read by the microscope. No intervals were allowed for recovery between the readings, which thus occupied a few minutes only. The specimens were always allowed to age for at least 24 hours before being removed and were then assumed to be at the temperature of the room. The own weight of the specimen was not taken into consideration, but E was calculated from the true stresses, which were calculated from the known loads per cm^2 of original cross-section on the assumption that the volume remained constant, so that the cross-section increased in the same ratio as the length was reduced.

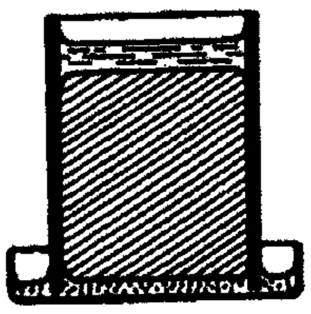
Fig. 1

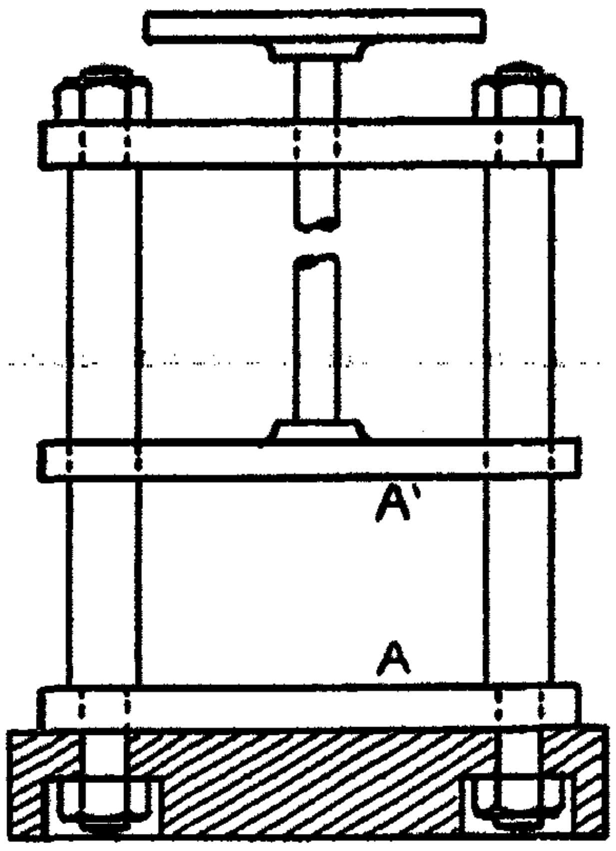

Fig. 2

Although the result was hardly in doubt it seemed to me desirable to ascertain on at least one specimen how the values of the modulus found by compression compared with those obtained in tension. A cylindrical specimen 25 mm dia. and 72 mm long was accordingly prepared in accordance with Sheppard's method and a central portion 49.8 mm long (which remained very approximately cylindrical during extension) marked off for observation. The results, as well as those obtained in compression on a specimen 31.5 mm dia., cast at the same time and otherwise treated exactly alike, are given in Table I.

The modulus apparently increases with increasing elongation and decreases with increasing compression. Whether the increase with tension is that observed by Poole (l. c.) and postulated on theoretical grounds (to which the decrease with increasing compression would seem to be a necessary corollary) or is the cumulative effect of the small irreversible deformation, need not be

TABLE I

Young's Modulus of Gelatin Gel (10 gm gelatin in 100 gm water) by Tension and Compression

(In this and all subsequent tables loads are given in gm, lengths in cm, and stresses and E in gm/cm²).

A. By Tension. (Temp. 17.0°)

Load	Length	Percent of original length	Stress	E
0	4.98	100	0	—
17.3	5.05	101.4	3.58	255
123.3	5.48	110.0	27.61	276
173.3	5.67	113.8	40.17	291
		B. By Compression. (Temp. 17.0°)		
0	2.70	100	0	—
157	2.50	92.6	18.7	250
357	2.27	84.0	38.5	239
557	2.06	76.3	54.8	231
757	1.90	70.3	68.9	230

discussed, as the exact determination of moduli is not one of the primary objects of this paper. I have, however, thought it of interest to compare a more extensive range of determinations with the values found in the literature and have therefore determined the moduli of four gels, respectively, containing 8, 10, 12.5 and 15 gm of gelatin (dried at 96° and kept in the vacuum desiccator until weighing) to 100 gm of water. The figures given below are the means of the values found at four loads:

Gelatin per 100 gm of water	8gm	10	12.5	15
E in g/cm²	283	367	480	665

Temperature 13.0°

The values are somewhat higher than those found by Leick (l.c.) and by Sheppard and Sweet (l.c.), who both worked with hard gelatins. The brand I used appears to be exceptionally hard, and has an ash content—0.6% of the dry weight—remarkably low for a commercial article.

Since the examination of gels other than gelatin by compression offers no difficulty, it appeared desirable to investigate two gels the mechanical properties of which, as far as I am aware, have not so far received any attention at all: agar gel and silicic acid gel.

A 5% agar gel was prepared according to the procedure described by Hatschek and Humphrey.[5] The (air-dry) agar was soaked in 20 times its weight of water, dispersed at 100° and then kept at about 90° for five or six hours. A greyish coagulum is formed, from which a portion of the clear sol can be decanted, while the rest can be filtered through a plug of glass wool. As agar gel can be cut quite satisfactorily, cylinders were simply cast in a brass

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[5] Trans. Faraday Soc., 20, Pt. 1 (1924).

tube corked at one end; after setting and cooling the cylinders of gel were pushed through so as to protrude a few mm and the meniscus cut off.

As the modulus of 5% agar gel turned out to be surprisingly high, only the higher loads were used. Two determinations are given below. No high degree of accuracy has been aimed at, the object of this investigation being rather to determine the order of magnitude of the modulus of gels not hitherto examined, as a factor to be taken into account in any theories of their structure.

TABLE II

Modulus of Agar Gel (5 gm in 100 gm water) Cylinder 3.5 cm dia.

A. Measured immediately after setting, *i.e.*, about 2 hours after casting

Load	Length	Percent of original length	Stress	E
0	3.598	100	0	—
321	3.560	98.94	33.0	3112
721	3.494	97.11	73.3	2535
921	3.458	96.11	92.0	2365

B. Duplicate specimen, cast at the same time as A and measured 24 hours afterwards

0	3.402	100	0	—
321	3.364	98.88	33.0	2946
521	3.338	98.12	53.1	2826
721	3.304	97.12	72.8	2527
921	3.270	96.12	92.0	2371

The two sets of determinations agree within the limits of experimental error and thus establish an interesting difference between agar and gelatin gels, the modulus of the former not increasing with time, while it is well known that the modulus of the latter does not attain its full value until the lapse of a period for which different values are given in the literature, the rate of increase probably depending on temperature to a greater extent than has been realized.

It is unnecessary to discuss at the moment whether the decrease in the modulus with increasing stress shown in both the series of measurements can be interpreted as evidence of fibrillar structure or is at least in part a consequence of permanent deformation, in which connection it should be mentioned that the specimens on removal of the maximum stress recover immediately to within about 98% of their original length. It is well known that water can be readily expressed out of agar gels, but with the stresses used and during the short time occupied by the whole series of readings no trace of exudation could be observed. If the specimen is left under the maximum stress (92 gm/cm^2), a slight dew is visible after 20 to 30 minutes. The 5% gel will support a stress of 350 gm/cm^2 without fracture and then loses water rapidly; quantitative data, which are ofin terest in another connection, will be given in a later portion of this paper.

Another gel, the elastic properties of which have received little attention, is silicic acid gel, though Prasad[6] has determined the modulus of a silicic acid gel (from which increasing quantities of water had been expressed mechanically) by bending a rod of it. For my purpose it was necessary to prepare perfect cylindrical specimens, a task of some delicacy. The two following procedures proved practicable: (a) the type of mould shown in Fig. 1 was employed, but the brass tube was replaced by a tube of filter paper impregnated with paraffin wax. The reaction mixture of sodium silicate and hydrochloric acid was poured in and covered with a thin layer of oil, a sample being set aside to allow observation of the setting and syneresis. When the gel had become firm the whole mould was placed in benzene which dissolved the paraffin in the paper, so that the gel cylinder could, with some care, be removed without injury. (b) An ebonite tube, vaselined inside and having turned edges, was clamped to a thick glass plate, also coated with vaseline, a little rubber grease being applied to the joint from outside to ensure its being perfect. The mould was filled as explained and the whole left until the control showed syneresis, when the glass plate was slipped off in its own plane, and the gel cylinder dropped out of the mould.

The mixture used throughout was: 35 cc of sodium silicate solution of sp. gr. 1.15 into 30 cc of 6 *N* hydrochloric acid (SiO_2 content of the silicate solution 102.9 gm per L.) The mixture set to a gel—*i.e.*, the vessel could be inverted without the surface of the gel showing any sagging—within 3 hours, and perceptible syneresis appeared after 5 or 6 hours.

By using method (b) I managed once to obtain a very perfect specimen which could be removed from the mould intact and submitted to investigation 6.5 hours after casting. The whole series is given in Table III to show the degree of accuracy attainable:

TABLE III

Young's Modulus of Silicic Acid Gel 6.5 Hours Old

Load	Length	Percent of original length	Stress	E
0	4.110	100	0	—
321	3.948	96.06	26.41	670
521	3.840	93.43	42.91	653
721	3.758	91.43	58.11	683
921	3.664	89.14	72.37	666
			Mean	668

About 10 seconds after the last reading had been taken, the gel was crushed. In a further series of measurements the gel was accordingly allowed to age longer before removal from the mould, *viz.*, 13 hours. This specimen was also very perfect and was used for following the increase of the modulus with age. The details of the measurements offer nothing new, and only the mean values of E are given in Table IV:

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[6] Kolloid-Z., 33, 279 (1923).

TABLE IV

Variation of Young's modulus of silicic acid gel with age

Age of gel in hours from time of casting	13	24	44	85	133
E	1113	1898	2031	2317	2550

The gel by the end of this series of measurements had developed a few cracks, and the investigation was discontinued, although the modulus was apparently still rising. The values are plotted in Fig. 3, in which the isolated point marked × shows the value for the gel 6.5 hours old. It falls fairly on the continuation of the curve found for the older gel and is some indication of the reproducibility of the results.

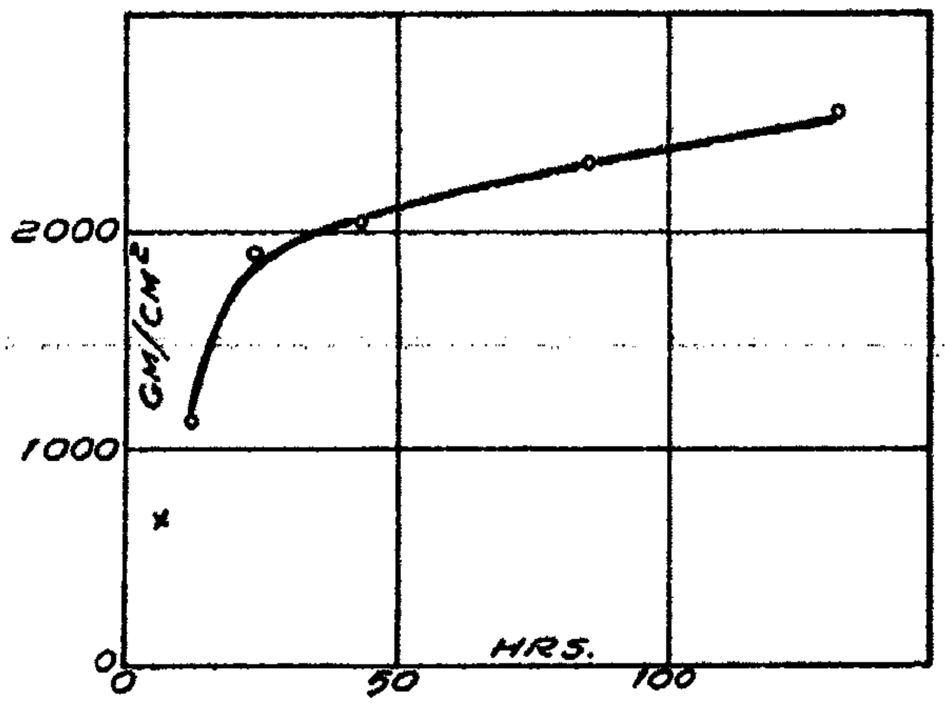

FIG. 3

The gel described in Table V continuously lost liquid by syneresis while kept in a saturated atmosphere. The initial and final weights and dimensions only are given below:

Initial	Final
Weight 51.588 gm Length 39.78 mm	Weight 43.898 Length 37.46
Diameter 38.00	Diameter 36.00

On a further specimen of exactly the same composition two sets of determinations only were made; the results were: E = 806, 8 hours after casting, and 2520, 83 hours after casting. Considering the uncertainty of the time required for setting the agreement with the values in Table IV is satisfactory.

One further gel, the elastic properties of which had struck me frequently in the course of other investigations, appeared to deserve detailed study, *viz.*, gelatin gel hardened by formaldehyde. Two cylinders were cast in the usual way from sols containing resp. 8 gm and 10 gm of gelatin (dried at 95° and kept in vacuum desiccator) in 100 gm of water. The moduli of both were again determined and found to be 283 and 366, in excellent agreement with the previous determinations. The two cylinders were then placed in a closed vessel of about 750 cc capacity, lined with several thicknesses of filter paper which was kept moistened with 40% formaldehyde solution. The specimens were weighed and the modulus determined at intervals; as copious syneresis occurs, the diameters were also re-measured at intervals and the loads per unit section recalculated. The results are shown in Table V:

TABLE V

Changes in Gelatin Gels during Hardening by Formaldehyde

8 percent gel

Time in hours	0	48	82	103	165	183	212
E	283	922	2206	2314	2391	2402	—
Weight	30.835	28.973	27.975	27.258	25.714	—	—
Ratio water/gelatin	12.50	11.70	11.26	10.94	10.27	—	—

10 percent gel

Time in hours	0	48	82	103	165	183	212
E	366	1379	2296	2559	4716	4982	5418
Weight	29.905	28.321	27.203	26.691	25.581	—	—
Ratio water/gelatin	10	9.49	8.97	8.76	8.38	—	—

Both specimens developed small cracks at 183 hours, and the investigation was therefore not continued beyond 212 hours. The moduli are plotted against time in hours in Fig. 4, and the curves show several striking features, such as the rapid initial rise of E, followed by an almost abrupt change to a very slow

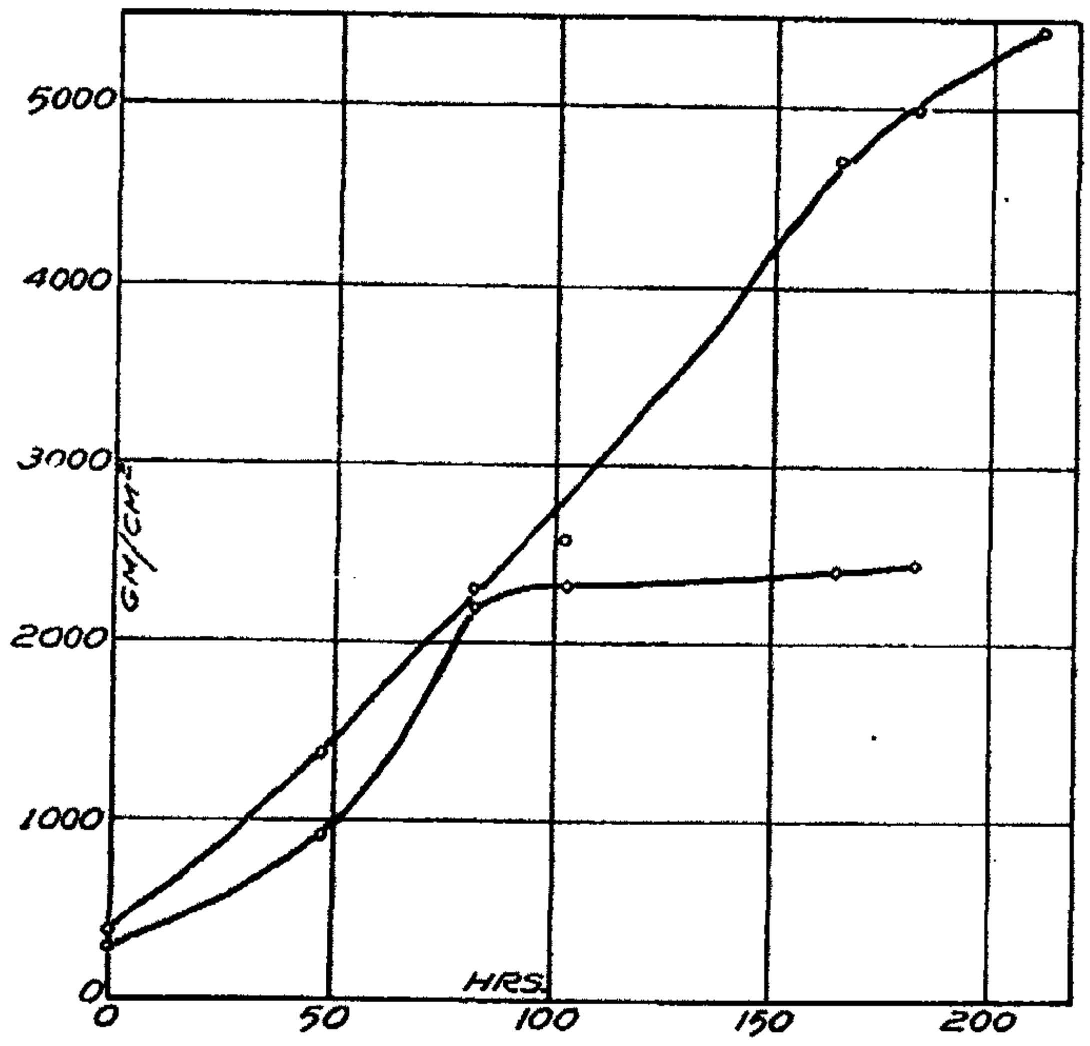

FIG. 4

rate of further increase, and the enormous difference between the 10 and the 8 percent gel as regards the absolute values of E. While there can be no doubt regarding the general course of the hardening process or the order of magnitude of E, the values of the latter are affected by an error due to the change in shape which the specimens undergo. As they lose water they do not retain their cylindrical shape, but, exactly like specimens drying in air, become barrel shaped with convex ends. Although within the range of the present experiments these changes are not too marked, they cannot be altogether allowed for merely by estimating (as has been done) a mean diameter and treating the specimen as cylindrical in the calculation of the stress. The values of the latter, and therefore of E, are likely to be too small, and with exact values the initial convexity of the E-T curves towards the T axis might disappear; the curves would then bear a marked resemblance to the curve for silicic acid gel.

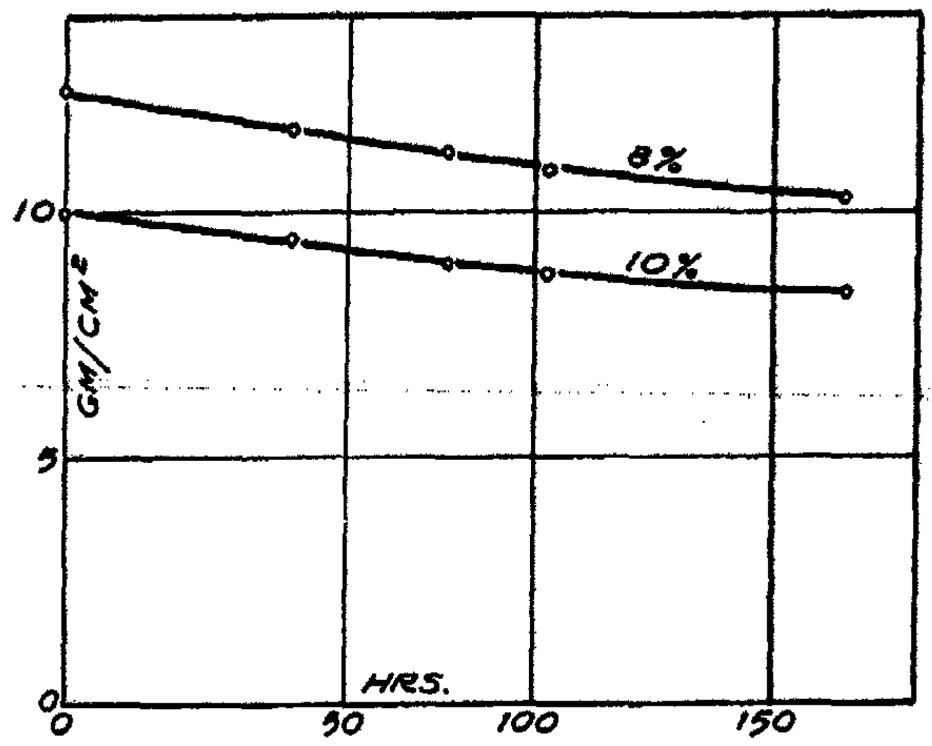

Fig. 5

The ratios water: gelatin for both gels are plotted against time in Fig. 5.

The accidental birefringence of deformed gelatin gels has been known for a considerable time, but for the present purpose the only paper in the earlier literature to which reference must be made is one by Reiger.[7] He determined the relaxation time of gelatin gels by observing the disappearance of double refraction at 29°—a temperature higher than the melting point of most brands of 10% gels, and one at which, according to Poole, the value of the Young's modulus of even a 24% gel falls to less than one tenth of the value at 11.5°. I showed, however, in 1920,[8] that mechanical relaxation may, at ordinary temperature, have become almost complete, while the optical anisotropy remains practically unchanged. This can hardly be explained on any assumption other than that of a change in structure during the transition from reversible to irreversible deformation, and this assumption has, indeed, been made by later authors who quoted this result. Poole writes: "The persistence of optical

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[7] Physik. Z., 2, 213 (1901).

[8] Hatschek: General Discussion, Faraday and Physical Socs. (H. M. Stationery Office, 1920).

strain after the disappearance of all mechanical stress seems capable of explanation by the foregoing theory (p. 132) in that if a molecule be removed by solution from a distorted fibril and then replaced by reprecipitation it will have given up its share of the stress. In this way when all the molecules in the fibril have been replaced the whole of the stress in the fibril will have disappeared, but the fibril will still retain its distorted form." Sheppard and McNally say: "It was shown by Hatschek that the optical anisotropy of gelatin jellies produced by stress does not decrease with the mechanical relaxation of the stress but remains, frequently, at the value corresponding to the first application of the stress. Hatschek has pointed out that this must be due to a permanent rearrangement of inner structure. This is in agreement with the view that gelation involves a condensation of ultimate molecular entities, which is followed by reorientation on application of stress."

In view of the peculiar character of the optical anisotropy produced by deformation it appeared of interest to examine whether gelatin gel under stress became anisotropic as regards its mechanical properties, such as the Young's modulus or tensile strength. It is of course easy to test these points on specimens which have undergone permanent deformation, and I have shown[9] by direct test that the tensile strength of a cylinder which had received a permanent elongation of 4% was over 80% higher than that of a cylinder in the original state. No such method is available for discovering possible anisotropy in the reversibly deformed gel, and the only way of doing so appears to be the observation of the lenticular gas bubbles produced in the gel while stressed.

I first drew attention to these bubbles in 1914[10] and then put the question whether the equatorial planes of the bubbles showed any orderly arrangement or were orientated at random—a question which I attempted to answer by the somewhat laborious procedure of determining the angles of inclination of a large number with an orthogonal system of coordinates. The problem fortunately assumed a simpler shape when I returned to it in 1929[9] and can now be stated as follows: We imagine, for the sake of simplicity, a small spherical bubble as existing in the isotropic gel and increase the pressure in it. A pressure will be reached when the tensile strength is exceeded and the gel is torn. The position of the fracture, *i.e.*, its angles with a system of axes, will be just as uncertain as will be the position of the break in a rod broken by tensile stress, and it therefore follows at once that if a large number of such bubbles is examined, their orientation must be a random one. It also follows at once that, if the tensile strength should be a minimum in one direction, the gel would be split at right angles to this direction, *i.e., the equatorial planes of the bubbles will be at right angles with the direction of minimum tensile strength.* As bubbles can readily be produced in a gel while it is reversibly deformed, this affords a means of discovering possible anisotropy during that period.

The gels used for these trials consisted of: 10 gm gelatin (air dry), 1 gm sodium hydrogen carbonate and 100 gm of water. Cylinders were cast in the same way as the specimens for the determination of Young's modulus by

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[9] Hatschek: Kolloid-Z., 49, 244 (1929).

[10] Hatschek: Kolloid-Z., 15, 226 (1914).

compression. The gas bubbles were formed by allowing the following solution to diffuse into the gel: 16 gm glacial acetic acid and 30 gm crystallized sodium acetate made up to one litre with water (about $0.26N$ in acid and $0.22N$ in acetate). The acetate is sufficient to repress the swelling due to the acid almost entirely: a specimen weighing 22.390 gm before immersion weighed 23.535 gm after diffusion was complete, the increase amounting to only 5%.

Gas bubbles were produced in cylindrical specimens during reversible and irreversible elongation and during reversible and irreversible compression. The specimens for the latter were, as already stated, cast so as to have plane end faces; for permanent deformation they were compressed in small screw presses and kept in a saturated atmosphere for 4-7 days. For studying the effect of reversible deformation the cylinders were compressed between glass plates in small wooden or ebonite frames and at once placed in the acid-acetate mixture. Fig. 6 shows the orientation of the bubbles during reversible (right) and after irreversible compression (left).

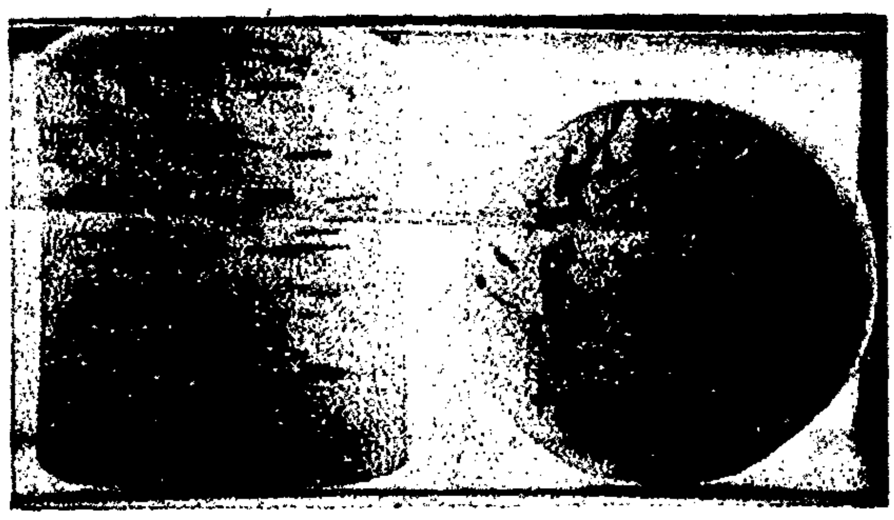

FIG. 6
Gas Bubbles in (right) reversibly, (left) irreversibly compressed gelatin gel

Specimens for tension were attached to beech wood blocks and stretched in ebonite frames; for reversible deformation they were at once placed in the acid-acetate mixture, while for irreversible deformation they were also kept for 4-7 days in a saturated atmosphere, then released from the wood blocks and placed in the acid-acetate solution. The results, which have been obtained quite uniformly on a large number of specimens, are as follows:

In *reversibly elongated* and *irreversibly compressed* cylinders the equatorial planes of the bubbles are *perpendicular* to the axis, *i.e.*, the *tensile strength is a minimum in the direction of the axis.*

In *irreversibly elongated* and *reversibly compressed* cylinders the equatorial planes of the bubbles are *parallel* to the axis, *i.e.*, the *tensile strength is a minimum in directions at right angles to the axis.*

The results can be put more generally and without reference to the shape of the specimen by saying that during *reversible deformation the direction of minimum tensile strength* is that in which the *linear dimension has been increased*, and *after irreversible deformation* that in which the *linear dimension has been reduced.* For both types of deformation therefore the direction of minimum tensile strength during reversible deformation is at right angles with that after irreversible deformation. In the interval of time during which the deformation changes from one type to the other, therefore, some rearrangement of the structure must take place.

For the moment I will not insist on the difficulty of bringing this result into harmony with the optical anisotropy, which remains unaltered during the transition from reversible to irreversible deformation. It appeared to me to be possible, that deformation, as it obviously causes a rearrangement, might sensibly affect the diffusion velocity, *i.e.*, that this might also become different in different directions. A series of experiments, which are here published for the first time, was therefore undertaken to test this point.

The principle and technique are again quite simple. If diffusion into a gel is allowed to take place through an orifice which may be regarded as a point, the boundary of the diffusion zone at any time is a sphere, provided the gel is isotropic for diffusion. Should the velocity in different directions become different as a consequence of deformation, the boundary surface would become oblate or prolate. As a sharp boundary of the zone is essential, it is necessary to use a diffusing solution which produces a precipitate with some solute present in the gel. I have found the formation of lead chromate the most suitable reaction for the purpose. The gels are made with a 1% solution of lead acetate—which incidentally acts as an excellent antiseptic—and a concentrated solution of potassium chromate allowed to diffuse into them.

Cylindrical test pieces with smooth plane ends, cast in the manner described earlier in this paper were used. A mask of transparent celluloid about 1.4 mm thick is squeezed to one end face so as to exclude air, the removal of which is easily checked by the absence of total reflection. A countersunk hole, 1 to 1.5 mm dia. drilled in the centre of the mask serves as the "point" source of diffusion: a drop of saturated potassium chromate solution is placed on it, care being taken not to trap an air bubble in the hole, and a few small crystals of the salt placed in it to keep the solution saturated.

The arrangement can be used for studying diffusion both during reversible and irreversible compression. For the former purpose an ebonite plate having a circular opening of 15 to 20 mm diameter is placed over the mask, to give sufficient access to the hole when the drop of solution is placed on it, and the whole is then compressed in a suitable framework. A diffusion zone of sufficient size can be obtained in about 48 hours in an 8 percent gel: if this were to be taken out of restraint, it would show an immediate small recovery followed by a still smaller one which continues for 24 hours or more. The diffusion zone formed during compression would therefore be distorted and, though its original profile could of course be found by calculation, a simpler way is to place the specimen and the press containing it in an atmosphere of formaldehyde, the supply of which can be so regulated that the specimen is hardened completely before being taken out.

Permanently deformed specimens were obtained by compressing cylinders in small screw presses kept in a saturated atmosphere for varying periods. On removal of the restraint there is an immediate partial recovery, followed by a further one, which is smaller in amount and takes a time of the order of 24 hours to complete itself. The following figures for cylinders of 9 percent gel give an idea of these effects:

Cylinders of 9% gel compressed to the following fractions of their original length

A	B	C	D
83.3%	81.3%	77.3%	74.7%

Removed from restraint after 48 hours. Percent of original length immediately on removal

89.2	87.2	85.9	84.8

24 hours later

89.9	90.4	89.6	87.7

The slight irregularity of the first two values in the last row suggests that the time for both the immediate and for the final recovery may be a function of the original stress, *i.e.*, the time may have been insufficient for complete recovery. The point, while interesting and deserving of investigation, is not material to the present enquiry, as the length of compressed specimens was always checked at intervals, and diffusion was not begun until it had remained constant for at least 24 hours.

The results are somewhat surprising or at any rate appeared so to me. *The diffusion zone both in reversibly and irreversibly deformed gels always is perfectly spherical.* This was established by the examination of a large number of specimens which were cut in half when the diffusion zone, as seen through the celluloid mask, had attained a diameter of at least 20 mm. Such a cross-section is shown in Fig. 7.

The gel therefore, as far as the *velocity of diffusion* in it, or its permeability, is concerned, *remains isotropic both during reversible and after irreversible deformation.*

The effects of deformation on various properties of gelatin gel are therefore:

1) Gels become optically anisotropic on deformation and remain so while the deformation becomes irreversible, the amount and "sign" of the anisotropy remaining substantially unaltered while the stress disappears.

2) Gels become anisotropic in respect of tensile strength, but the direction of minimum tensile strength during reversible deformation is at right angles to that after irreversible deformation. In *reversibly deformed gels the direction of minimum tensile strength is that in which the linear dimension of the specimen has been increased, while in permanently deformed gels it is the direction in which the linear dimension has been reduced.*

3) Gels remain *isotropic for diffusion* both during reversible and after irreversible deformation.

A large number of investigators (Sheppard, Poole, Northrop, Kunitz, Lloyd and Pleass) agree in postulating for gelatin a structure consisting of fibrils orientated at random and in assuming that the elastic behaviour of the gel is simply the elastic behaviour of such a network, the liquid phase playing a part merely in such phenomena as "creep." As the best test of a hypothesis is its application to new phenomena, it will be convenient to examine what effect the deformation of such a structure would have on the three properties studied by me.

The persistent isotropy in regard to diffusion velocity is no doubt easiest of explanation. It may be taken as established that diffusion in gels of low or moderate concentration is not much slower than in the pure dispersion medium; if a fibrillar structure is assumed it must therefore be taken to occupy a comparatively small portion of the total volume. In that case it is easy to understand that deformation would not very materially affect the cross section available in any direction and would accordingly not cause perceptible anisotropy.

The effects of deformation on tensile strength are much more difficult to interpret, and it is necessary to discriminate between reversible and irreversible deformation. The former reduces tensile strength in the direction of dilatation, a result intelligible even without any assumption concerning structure: the material is already stretched in that direction and the additional tensile stress required to cause rupture is smaller.

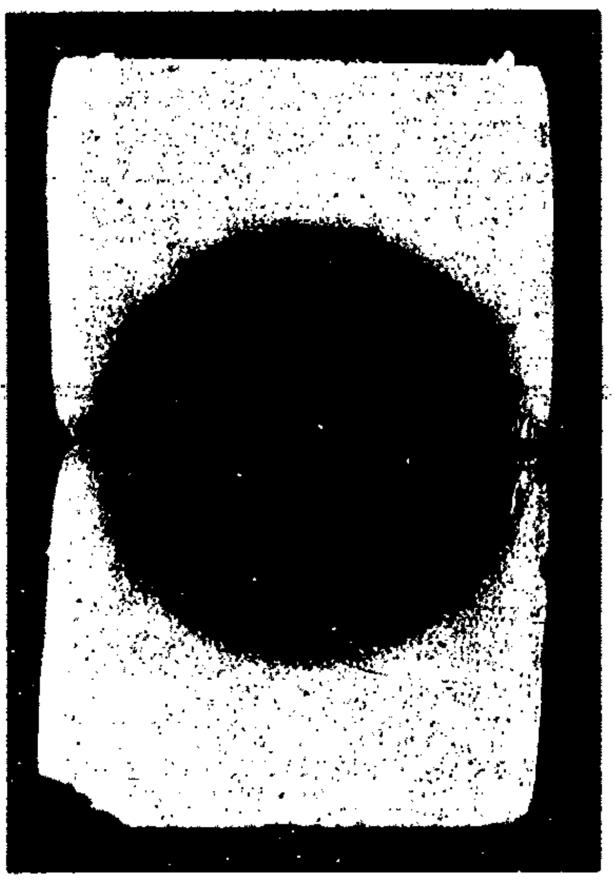

Fig. 7

Diffusion in Cylinder compressed reversibly to 83% of original length. Specimen cut through axis and halves placed together to show the sphericity of the diffusion zone

The converse effect, that after irreversible deformation the tensile strength is greatest in the direction of dilatation must be explained in terms of structure and on the assumption that the tensile strength of the gel, like its elasticity, is merely that of the fibrillar network. The first point to be remembered is that it does not become merely a *relative* maximum, but that the tensile strength of permanently stretched specimens is *absolutely* greater than that of undeformed specimens of equal age. The aggregate cross-sections with a plane perpendicular to the stress can hardly be assumed to increase while deformation becomes permanent: the diffusion experiments, for what they are worth, provide evidence that the passage ways remain equal in all directions. It must however, be borne in mind that, when a structure consisting of fibrils orientated at random is ruptured by tensile stress, the rupture of individual fibrils will be caused by a combination of tensile and shearing stress, the latter prevailing more and more as the angle of the fibril with the direction of stress increases. Now the fibrils must be built up of elements, the name and nature of which are immaterial at the moment; the simplest general structure we can assume is a cylinder built up from equal elements with oblique parallel ends

(Fig. 8a). If the joints are easier to shear than the material of the elements, it is obvious that a rotation of the cylinder through 90° (from a to b) will reduce its resistance to a shearing stress in the direction of the arrow. The assumption that such a rotation occurs is of course purely *ad hoc*, and is an attempt to keep within the theory which ascribes the mechanical properties to a fibrillar network, and to suggest a mechanism consistent with the diffusion isotropy and easily reconcilable with the unchanging optical anisotropy.

Before, however, great weight can be attached to such a hypothesis, much further investigation of the actual transition from reversible to irreversible deformation is required. The gas bubble method gives unambiguous results for the two extreme states, and I have made many attempts to apply it to the intermediate stages. The progress of orientation, however, cannot be traced except by laborious statistical methods which I have not yet found time to apply. An interesting question, which may be settled incidentally, is the following: in the extreme stages the gel is, apparently, uniaxial. Does it become biaxial or isotropic at some stage during the transition? Since the axes of minimum strength in the extreme states are at right angles to each other, either case would seem to be possible.

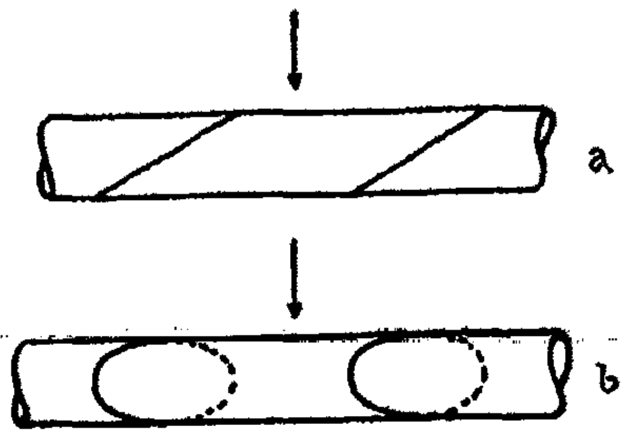

FIG. 8

It is convenient to discuss at this point the gelatin gel hardened by formaldehyde. The specimens examined contained initially 8 gm and 10 gm of gelatin to 100 gm of water, and the moduli were 283 and 366 gm/cm.^{2} After 165 hours the moduli had increased to 2391 and 4716 gm/cm.^{2} During this time both gels had lost water, and comparison between the natural and hardened gel must be based on the gelatin content of the latter at the time of measurement. The ratios: water/gelatin after 165 hours were 10.27 and 8.38 resp., and the moduli of gels of natural gelatin of these concentrations, obtained by graphical interpretation from the data previously given are 355 and 452 gm/cm.^{2} By the reaction with formaldehyde the modulus of the (originally) 8% gel had therefore increased in the ratio 2391/355 = 6.73, and that of the (originally) 10% gel in the ratio 4716/452 = 10.42.

Interpretation of these figures is made difficult by the uncertainty how far they are from equilibrium values, but is not easy even on the assumption, which the graphs seem to support, that the ratio of the moduli at equilibrium does not differ greatly from that at 165 hours. It is not probable that any structure present in the original gel can undergo substantial rearrangement at ordinary temperature; the hardened specimens when examined in polarized light show a certain amount of strain, but no more than is exhibited by gel specimens which have lost the same fraction of their water content by drying in air. Failing rearrangement of structure, the increase in the modulus of the hardened gel must be due to an increase in the modulus of the fibrillar material. In that event (assuming, of course, saturation with CH_2O) the ratio

$$\frac{\text{Modulus of hardened gel}}{\text{Modulus of natural gel of same gelatin content}}$$

should be the same for all concentrations. This, as has been shown, is very far from being the case, and the hypothesis that the elastic behaviour of the gel is merely the behaviour of an elastic net work seems inadequate. In this connection the considerable loss of water during hardening may be significant. On the basis of accepted theory it may be explained by an increase in the modulus of the net work without a corresponding increase in the osmotic pressure of the liquid phase which is assumed to balance the elastic forces. This may account qualitatively for the loss of liquid, though much further work would be required to determine whether it does so quantitatively; in any event it does not, without some subsidiary hypothesis, provide an explanation of the great difference between the relative increases in the moduli of the two gels.

Problems of equal difficulty are raised by the data—scanty as they are so far—on the elastic behaviour of agar and silicic acid gels. The first thing that requires explanation in terms of structure is the high absolute value of both moduli, and the rapid increase with time exhibited by the modulus of silicic acid gel. This ageing effect also raises the fundamental problem played by water, since the only ready explanation of the increase with time appears to be displacement of water from one phase to the other. With agar there is the further possibility that investigation of the temperature coefficient of elasticity may throw light on this point, and on the mechanism of water retention which in this gel appears at first sight to be radically different from that in gelatin.

While the first approach to the subject thus seems to raise more questions than it answers, I have little doubt that further study of the elastic behaviour of gels, and possibly of their tensile strength, supplemented by diffusion experiments over a large range of conditions, should afford us a deeper insight into their structure than we possess at present.

London, England.

X-RAY STUDIES ON THE HYDROUS OXIDES

I. Alumina

BY HARRY B. WEISER AND W. O. MILLIGAN

The addition of a base to a solution of an Al salt gives a highly gelatinous precipitate usually designated as $Al(OH)_3$. While considerable evidence indicates that the gelatinous mass when first formed is hydrous Al_2O_3, and not an aluminum-oxide hydrate such as $Al_2O_3 \cdot 3H_2O$, a number of older as well as more recent investigations point to the existence of a hydrate or a series of hydrates in the freshly precipitated gel.

A critical survey of the evidence for and against the existence of definite hydrates in precipitated alumina was made 6 years ago.[1] Since that time the situation has been complicated by the interpretation put on vapor pressure and x-ray data obtained more especially by Hüttig and Willstätter. In the present article are given: (A) An historical summary in tabular form of vapor pressure and x-ray data on (1) precipitated alumina and (2) the trihydrate of alumina. (B) An x-ray study of (1) Hüttig aluminas, (2) Willstätter aluminas, (3) precipitated alumina aged at 100°, (4) aged alumina decomposed by heat, (5) alumina formed by the decomposition of hydrated aluminum chloride, (6) alumina formed by the decomposition of gibbsite (7) artificial gibbsite.

A. Historical

(1) *Precipitated Alumina.*

Composition. The precipitate formed by the interaction of NH_4OH and a soluble Al salt will henceforth be designated as precipitated alumina. Different investigators have assigned various formulas to the precipitate dried in different ways. Some typical results are summarized in Table I. It is apparent that while certain investigators, especially van Bemmelen and Shidei, question the existence of hydrates, others, notably Hüttig and Willstätter, believe that a part of the water is chemically bound in the orthodox sense to give definite compounds. The work of Willstätter and of Hüttig will receive critical consideration in the experimental part of this paper.

The vapor pressure data of Shidei on precipitated alumina commands special attention. He treated $AlCl_3$ solution with NH_4OH, washed the resulting precipitate by decantation several times and then dialyzed it for 11 days at 50°-60°. The resulting precipitate was free from Cl^- and SO_4^{--} but still contained a trace of ammonia. The vapor pressure curve at constant temperature for this precipitate was determined in a specially designed apparatus. Extreme care was taken to obtain equilibrium values which in some experiments required over 70 days. The curve reproduced in Fig. 1 shows clearly

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

TABLE I

Composition of Precipitated Alumina

Investigator	Method of drying	Composition mols H_2O per mol Al_2O_3	Investigator's conclusions
Van Bemmelen[1]	Air-dried	4.3 to 4.5	No definite hydrates except possibly a trihydrate
Carnelley and Walker[2]	Air-dried	5	Either no hydrates or a very large number of hydrates
	At 65°	3	
	At 160–200°	2	
	At 250–290°	1	
	At 850°	0	
Allan[3]		Precipitated Cold Hot	Composition determined by method of drying
	Air-dried	3.03 2.89	
	Over H_2SO_4	2.020 2.04	
	At 100° C	2.015 1.88	
Guichard[4]	Air-dried	6.59	The di- and trihydrates exist in the cold precipitate
Hüttig and coworkers[5]	Aged under varying conditions	3 to 1	A series of definite hydrate are formed
Willstätter and coworkers[6]	Pptd. and dried under varying conditions	3 to 1	Definite hydrates are formed
Shidei[7]	Varying pressure	See Fig. 1	No hydrates

that no definite hydrates are formed under the conditions of Shidei's experiments. It was assumed that the water is present in the form of a solid solution in the alumina; but it is more probable that the water is retained by adsorption forces on the surface of finely-divided crystals.

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[1] Rec. Trav. chim., 7, 75 (1888).
[2] J. Chem. Soc., 53, 87 (1888).
[3] Chem. News, 82, 75 (1900).
[4] Bull., (4) 37, 251, 381 (1925); 39, 190 (1926).
[5] Z. anorg. Chem., 171, 323 (1928); 187, 1 (1930).
[6] Ber., 56, 149, 1117 (1923); 57, 58, 1087 (1924); 58, 2448, 2458 (1924); 64, 1697 (1931).
[7] Mem. Coll. Sci. Kyoto, 9a, 42 (1924).

X-Ray Data. A number of investigators have examined precipitated alumina by x-ray diffraction methods. Haber[1] obtained no diffraction effect with a precipitate formed in the cold and air-dried, but observed one broad band in the precipitate from an ultrafiltered alumina sol prepared by Crum's method. He concluded from this that the gel is amorphous when thrown down in the cold but gradually assumes an ordered structure. Frick and Weaver,[2] on the other hand, observed one broad diffraction band from a precipitate formed at room temperature and a weak pattern from one thrown down at 100°. Böhm[3] obtained a well-defined pattern which he described as similar to some "bauxites" in a precipitate thrown down at 100°. These qualitative observations have been extended by more recent quantitative work which has been summarized in Table II and Fig. 2. Because of the similarity in the x-radiograms from a number of the samples, it is necessary to reproduce only a few of them. The numbers in the last column of the table correspond to the numbers of the x-ray diagrams shown in the figure. It will be noted that all of Biltz and Lehrer's samples yield similar but not identical diffraction effects. Rooksby examined a number of preparations formed with varying concentrations of ammonium hydroxide at both room temperature and at 100°. The x-ray patterns from the several samples were identical except for a slight variation in the width of the lines, showing that the conditions of preparation influence the particle size. The lines were quite diffuse but the positions were the same with the product formed by the thermal decomposition of gibbsite. Further discussion of Rooksby's results will be given in a later section.

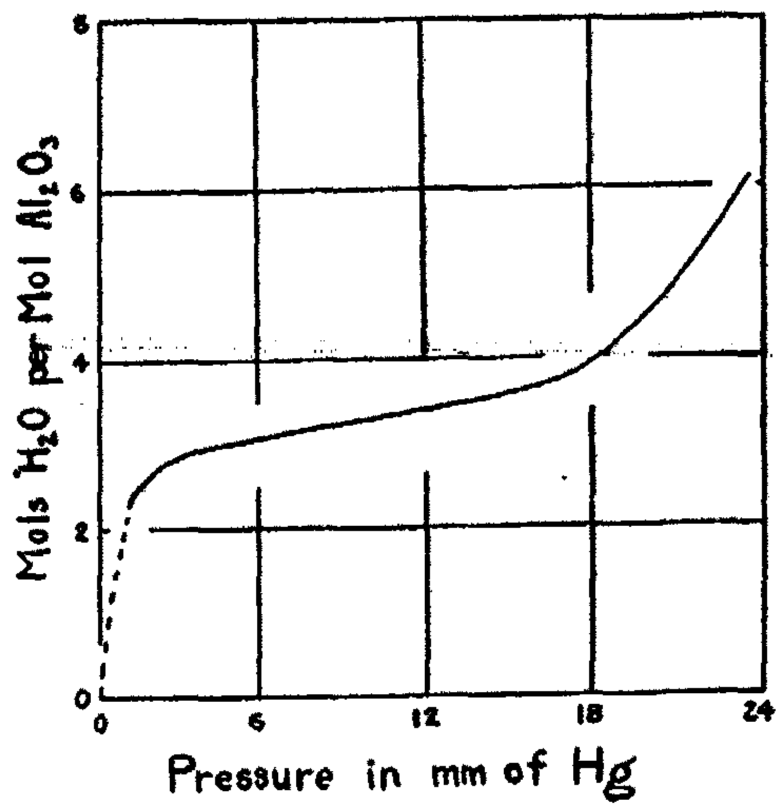

FIG. 1

Vapor Pressure-Composition Diagram for Precipitated Alumina (after Shidei)

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[1] Ber., 55, 1727 (1922); Böhm and Niclassen: Z. anorg. Chem., 132, 1 (1920).

[2] Z. anorg. Chem., 136, 321 (1924).

[3] Z. anorg. Chem., 149, 203 (1925).

TABLE II

Precipitated Aluminas used in X-Ray Diffraction Studies

Investigator	Treatment	Composition mols H_2O per mol Al_2O_3	No. in Fig. 2
Biltz and Lehrer[1]	Dried:		
	At 100°	1.03	–
	With liquid NH_3	1.15	–
	With liquid NH_3	2.995	1
	With acetone	2.88	2
	With liquid NH_3	2.04	–
	With liquid NH_3	1.00	3
	With acetone	1.00	–
	With acetone	1.71	–
	With liquid NH_3	1.49	–
	With liquid NH_3	1.98	4
	With acetone	3.16	–
	With acetone	2.39	–
	With acetone	2.55	–
	With liquid NH_3	2.98	5
de Jong[2]	precipitated and dried at 40–45°	—	6
	" " " " 100°	—	–
Rooksby[3]	Dehydration of Gibbsite at 250°	1	7
	Precipitated at 20°	–	Similar to 7
	" " 100°	–	" " 7

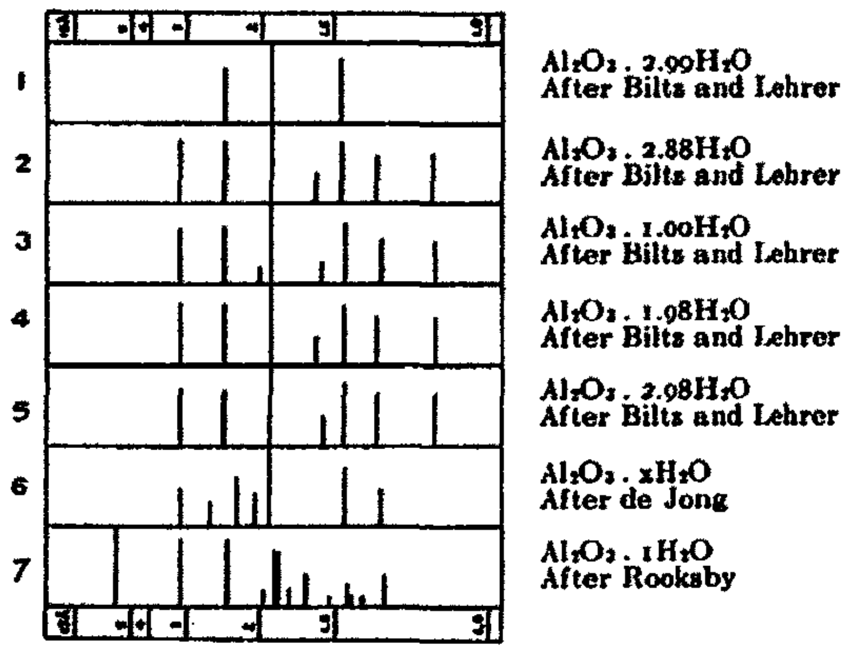

FIG. 2

X-Ray Diffraction Diagrams of Precipitated Aluminas

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[1] Z. anorg. Chem., **172**, 302 (1928).

[2] Z. Krist., **66**, 303 (1928).

[3] Trans. Ceram. Soc. England, **28**, 399 (1929).

(2) The Crystalline Trihydrate.

The mineral gibbsite occurs in nature in the form of well-defined crystals. The artificial preparation of this compound has been accomplished in a variety of ways. Thus Bonsdorff[1] and Bayer[2] dissolved alumina gel in KOH and allowed the solution to stand in a closed vessel until crystals appeared. Similarly, Goudriaan[3] dissolved Al in NaOH and allowed the solution to stand in the air, and Fricke[4] passed CO_2 slowly into cold alkali aluminate solution or slowly hydrolyzed the aluminate by dilution. While the composition of the several preparations corresponds to the formula $Al_2O_3 \cdot 3H_2O$, there is a difference of opinion as to whether the artificial preparations are identical with gibbsite. This point has been investigated by x-ray diffraction methods. The results are summarized in Table III and a number of x-ray diagrams are reproduced in Fig. 3. Except for the results of Biltz and Lehrer, the evidence is fairly conclusive that the artificial preparations are either identical with

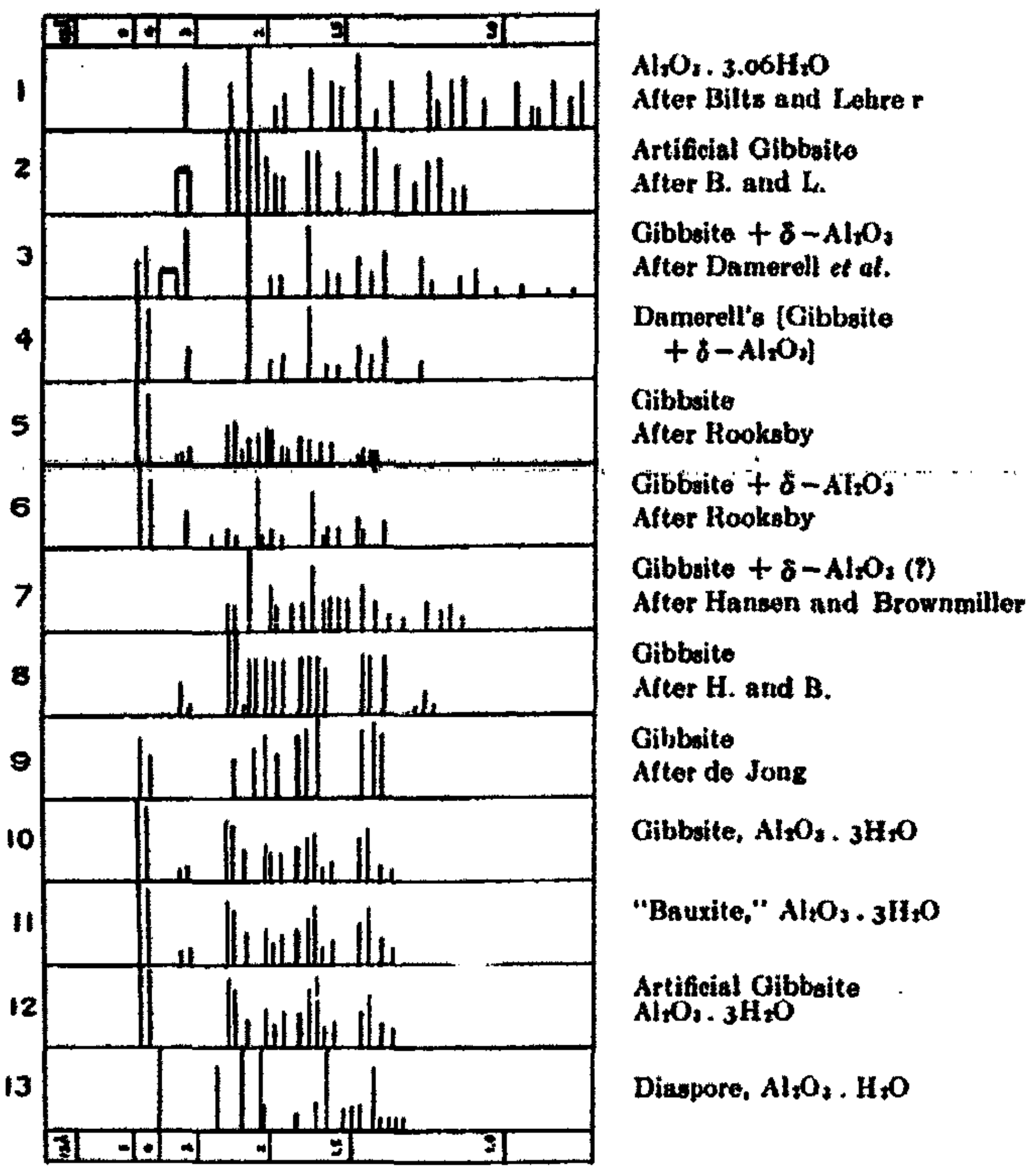

FIG. 3

X-Ray Diffraction Diagrams of Natural and Artificial Gibbsites, etc.

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[1] Pogg. Ann., **27,** 275 (1833).

[2] Chem.-Ztg., **12,** 1209 (1889).

[3] Proc. Roy. Akad. Amsterdam, **23,** 129 (1921).

[4] Z. anorg. Chem., **175,** 249 (1928); **179,** 287 (1929).

TABLE III

Artificial Gibbsite and Similar Preparations

Investigator	Method or sample	X-ray pattern obtained	No. in Fig. 3
Biltz and Lehrer[1]	Precipitated by NH_4OH at 70° and dried with acetone	Unlike gibbsite	1
	Bonsdorff's method	Somewhat like gibbsite	2
Damerell[2]	Precipitated alumina aged in cold	Similar to gibbsite	3
Weiser and Milligan	Damerell's sample	Similar to gibbsite	4
Frick and coworkers[3]	Slow hydrolysis in cold of alkali aluminate	Identical with gibbsite	–
	Rapid hydrolysis of alkali aluminate	Similar to some "bauxites"	–
L. H. Milligan[4]	Bayer's method	Identical with gibbsite	–
Rooksby[5]	Mineral gibbsite	Gibbsite pattern	5
	Goudriaan's method	Somewhat different from gibbsite	6
Hansen and Brownmiller[6]	Goudriaan's method	Similar to Rooksby's results	7
	Mineral gibbsite	Gibbsite pattern	8
de Jong[7]	Mineral gibbsite	Gibbsite pattern	9
Weiser and Milligan	Mineral gibbsite	Gibbsite pattern	10
	Mineral "bauxite"	Gibbsite pattern	11
	Bonsdorff's method	Gibbsite pattern	12
	Goudriaan's method	Gibbsite pattern	12
	Mineral diaspore	Diaspore pattern	13

gibbsite or are gibbsite mixed with more or less of a crystalline form of alumina which has been termed δ-Al_2O_3 (See experimental part). Our x-radiograms of (1) a mineral gibbsite, (2) a mineral "bauxite" and (3) artificial gibbsites obtained by Bonsdorff's and Goudriaan's methods were identical as nearly as could be determined (Fig. 3: 10, 11, and 12). It is not obvious why the

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[1] Z. anorg. Chem., 172, 302 (1928).

[2] Damerell: J. Phys. Chem., 35, 1061 (1931); Damerell, Hovorka, and White; 36, 1255 (1932); Tartar and Damerell: 36, 1419 (1932).

[3] Z. anorg. Chem., 175, 249 (1928); 179, 287 (1929).

[4] J. Phys. Chem., 26, 247 (1922).

[5] Trans. Ceram. Soc. England, 28, 399 (1929).

[6] Am. J. Sci., (5) 15, 225 (1928).

[7] Z. Krist., 66, 303 (1928).

x-radiograms of Bonsdorff's and Goudriaan's artificial gibbsites obtained by Biltz and Lehrer, Rooksby, and Hansen and Brownmiller should exhibit the differences shown in Fig. 3. As will be pointed out in the section "Synthesis of Gibbsite" in the experimental part of this paper, it is probable that the differences are due in part to variations in the conditions of preparation of the several samples.

B. Experimental

(1) *Preparations according to Hüttig's Procedures.*

Hüttig and coworkers[1] prepared a number of alumina precipitates and studied them by isobaric dehydration and x-ray diffraction methods. The gel freshly precipitated in the cold, appeared to be amorphous and to lose water continuously with increasing temperature. On standing at ordinary temperatures the fresh gel went over gradually into $Al_2O_3 \cdot 3H_2O$. According to Hüttig the transformation was not direct; but a series of crystalline intermediate hydrates between $Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3H_2O$ was believed to form. Every member of this series of hydrates manifested its individuality by a definite step-like curve.

Hüttig and Kostelitz recognized two more or less separate and distinct ageing processes; (a) gelatinous alumina, which consists of alumina and adsorbed water, reacts with the adsorbed water to form a series of compounds ending with $Al_2O_3 \cdot 3H_2O$; (b) a lower alumina hydrate, assumed to be $Al_2O_3 \cdot H_2O$ (diaspore) with adsorbed water, reacts with the adsorbed water giving a series of compounds with $Al_2O_3 \cdot 3H_2O$ as the final product. These two processes are represented in Figs. 4 and 5, respectively. In Fig 4 the transformation is from I → II → III → IV in which I represents the non-crystalline $Al_2O_3 \cdot xH_2O$, II and III, intermediate hydrates and IV, gibbsite. The second process is represented in Fig. 5 in which the changes are from 1 which is the curve for the monohydrate (disapore) through 2, 3, 4, and 5, the curves for intermediate hydrates, to 6, the curve for gibbsite.

X-radiograms of the several products were found to exhibit differences each from the other. This was likewise interpreted to mean that each was a definite chemical individual intermediate between non-crystalline alumina monohydrate on the one hand and trihydrate on the other.

It is well known that differences in the mode of precipitation of a definite material may influence the particle size and thus the width (sharpness) of the lines on the x-ray diffraction pattern; but differences in the position and relative intensities of the lines require further explanation. The differences in the position may be accounted for as the result of (1) formation of a solid solution with water in varying amounts, (2) experimental errors inherent in the apparatus employed, (3) error in measuring the positions of the lines due to a failure to calibrate the film with a material of known spacings (4) the samples being mixtures rather than pure definite compounds as Hüttig and Kostelitz assumed their intermediate products to be. Of course, no signifi-

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[1] Hüttig and Wittgenstein: Z. anorg. Chem., **171**, 323 (1928); Hüttig and Kostelitz: **187**, 1 (1930).

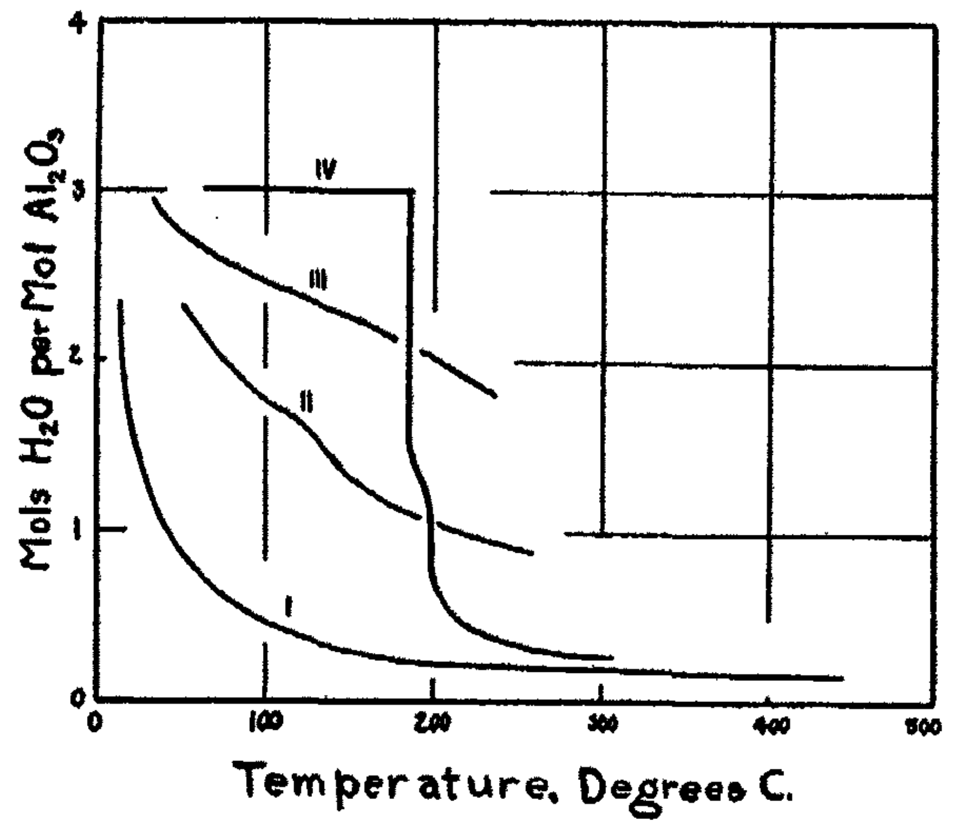

FIG. 4

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, I)

cance can be attached to slight differences in visually estimated intensities. Unfortunately Hüttig's x-ray data are recorded only in chart form on a small scale, and it is altogether impossible to make any accurate comparisons with the results of other people.

Preparation and Treatment of Samples. In the present investigation samples of precipitated aluminas were prepared and aged as nearly as possible in accord with the procedures of Hüttig and Kostelitz. Both the *K* and *L* series of samples were investigated. To prepare the former, one liter of 2 *N* NH_4OH was added with stirring to 90 g of $AlCl_3 \cdot 6H_2O$ dissolved in 200 cc of

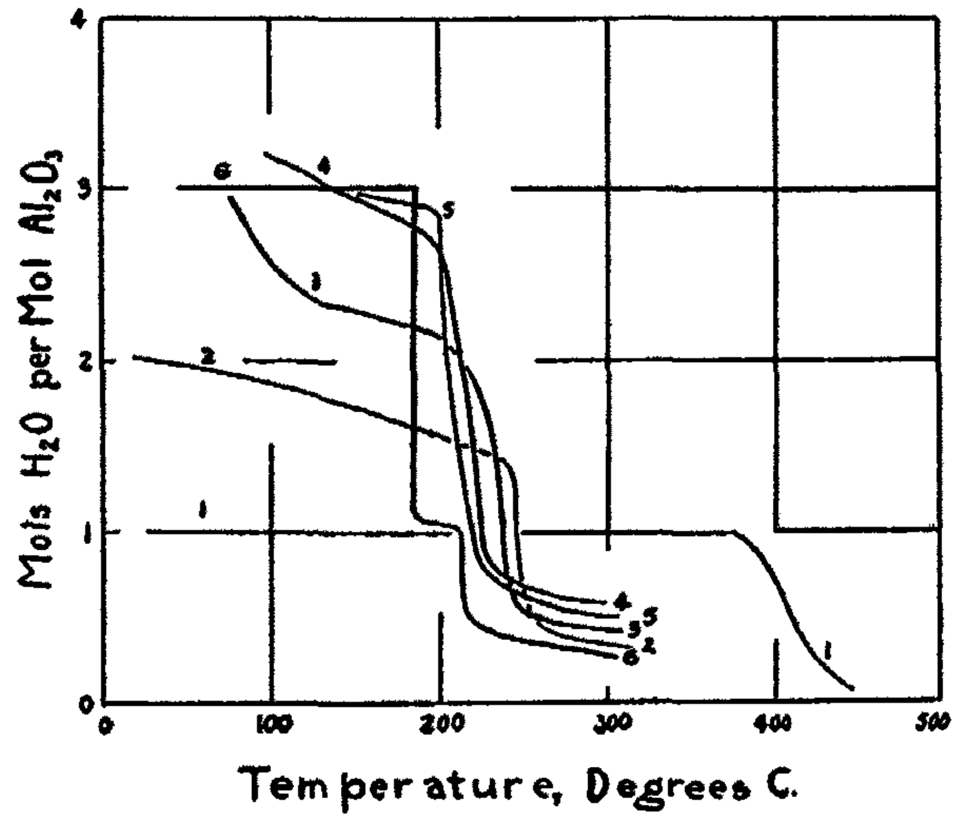

FIG. 5

Temperature-Composition Curves of Precipitated Alumina (after Hüttig, II) water at room temperature. The resulting hydrous precipitate was placed in 250 cc wide-mouthed bottles and washed ten times by the aid of the centrifuge using 200 cc portions of water. At the conclusion of the washing, the gel was almost chloride free and sol formation had begun. The sample was divided into five parts and aged as shown in Table IV.

The *L* samples were made by adding 48 cc of 25% NH_4OH at 48°C to 548 cc of a solution containing 118 g $Al_2SO_4 \cdot 18H_2O$ and 37.6 g of NH_4Cl. The resulting precipitate was washed as above described and four samples were aged as given in Table IV.

TABLE IV

Ageing of Precipitated Aluminas

Samples	Method of Ageing
K_1 and L_1	In a closed desiccator over 10% H_2SO_4; K_1, 15 weeks and L_1, 18 weeks
K_1''	Same as K_1 for 29 weeks
K_2 and L_2	In the open air but protected from dust for 27 weeks
K_3 and L_3	In a closed desiccator for 31 weeks
K_4 and L_4	Over water in a closed desiccator for 22 weeks

X-Ray Examination. The samples above described were air-dried, powdered, and placed in a thin nonex capillary tube, one end of which contained a sample of very pure NaCl which was used to calibrate the film. X-ray diffraction patterns were obtained with the General Electric x-ray diffraction apparatus. The results are given in Table V, and the diagrams of the x-radiograms are shown in Fig. 6. The interplanar spacings $d_{hkl}/n = D$ are expressed in Ångstrom units; I represents the relative, estimated intensity on such a scale that 10 is the most intense line. In the figure the x-ray pattern of gibbsite and of what we have termed δ-Al_2O_3 are included for the purpose of reference.

It is impracticable to discuss these data until the evidence for the existence of δ-Al_2O_3 is given. It is significant however that Hüttig's *K* samples formed in the cold are all quite similar and are probably mixtures of gibbsite with δ-Al_2O_3. The *L* samples formed at higher temperature give patterns almost identical with that of δ-Al_2O_3 except L_3 which is similar to the *K* samples. It is not apparent why the gibbsite structure should have started in but one of the *L* samples. However, the temperature of formation was not sufficiently high to preclude this possibility and one might expect it to happen occasionally. It is altogether probable that if L_3 has been aged a longer period, it too would have changed in part into gibbsite.

(2) *Preparations according to Willstätter's Procedures.*

Samples of several aluminas were made according to the procedures of Willstätter and coworkers and were examined by the x-ray diffraction method.

Preparation of Samples. A. One liter of a solution containing 100 g of $Al_2(SO_4)_3 \cdot 18H_2O$ at 100° was added to one liter of 6 *N* NH_4OH at 50° with

TABLE V

K_1'		K_1''		K_2		K_3		K_4		L_1		L_3		L_4	
D	I	D	I	D	I	D	I	D	I	D	I	D	I	D	I
4.65	10	4.76	9	4.75	8	4.79	10	4.75	10	3.18	7	4.79	10	3.18	7
4.32	10	4.31	9	4.36	8	4.34	10	4.39	9	2.36	8	4.39	9	2.36	8
3.22	3	3.18	4	3.19	2	3.19	4	3.22	5	1.85	10	3.22	5	1.85	10
2.36	4	3.46	2	2.39	2	2.47	2	2.47	3	1.43	6	2.47	3	1.43	6
2.22	10	2.37	3	2.22	10	2.37	3	2.37	3	1.31	4	2.37	3	1.31	4
2.00	2	2.26	1	1.99	1	2.26	1	2.22	10	1.13	2	2.22	10		
1.87	2	2.22	10	1.90	1	2.22	10	2.01	2			2.01	2		
1.71	6	1.99	1	1.789	1	2.00	2	1.89	2			1.89	2		
1.55	1	1.885	1	1.721	5	1.89	1	1.72	8	L_2		1.72	8		
1.44	5	1.770	1	1.436	3	1.77	1	1.64	1			1.64	1		
1.38	3	1.709	7	1.390	2	1.72	7	1.60	1			1.60	1		
1.33	4	1.639	1			1.65	1	1.56	1	3.18	7	1.56	1		
1.21	1	1.589	1			1.60	1	1.44	3	2.36	8	1.44	3		
1.16	1	1.550	1			1.55	2	1.39	2	1.85	10	1.39	2		
1.13	1	1.431	4			1.44	3	1.33	2	1.43	6	1.33	2		
		1.389	3			1.39	3	1.21	1	1.31	4	1.21	1		
		1.327	4			1.33	4			1.13	2				
		1.204	2			1.21	2								

vigorous stirring, after which steam was passed into the mixture for 5 hours, adding more ammonia from time to time. The resulting precipitate was washed free from sulfate and chloride by ordinary decantation and finally by the aid of the centrifuge. A portion of the sample was dried over P_2O_5 for 30 days and then contained 21.72% water. Willstätter and Kraut found a composition approximating $Al_2O_3 \cdot 2H_2O$ for a similar sample dried over H_2SO_4.

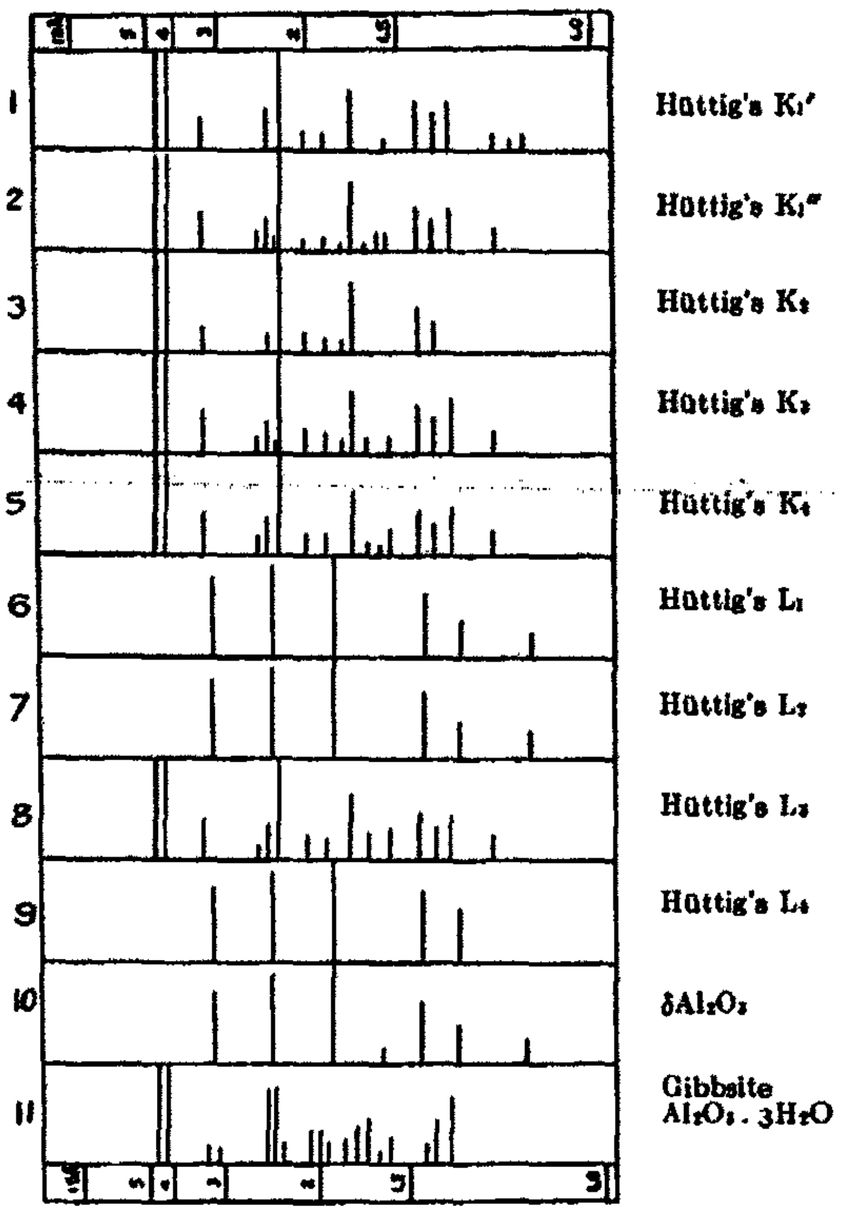

Fig. 6

X-Ray Diffraction Diagrams of Precipitated Aluminas prepared according to Hüttig's Procedures

B. This preparation was precipitated like *A*, but instead of passing in steam, it was heated on a steam bath for 30 minutes at 65°, then washed nearly free from sulfate and chloride.

D. About 65 g of alumina (calculated as $Al(OH)_3$) were dissolved in a solution of 70 g of KOH in 450 cc of water. The resulting solution was filtered, diluted to 5 liters, and CO_2 passed in rapidly. After thorough washing the sample was dried over P_2O_5 for 30 days.

New A. Willstätter, Kraut, and Humme[1] have recently modified the procedure for preparing the *A* sample which is claimed to give the definite hydrate $Al_2O_3 \cdot 2H_2O$. A sample was made according to this procedure: A solution of

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[1] Ber., 64, 1697 (1931).

250 g $Al_2(SO_4)_3 \cdot 18H_2O$ in 750 cc of water was warmed to 48° and poured rapidly with vigorous mechanical stirring into 2.5 liters of 15% by weight NH_4OH also at 48°; the temperature rose to about 50°. The resulting mixture was stirred for 30 minutes, and diluted to 12 liters with distilled water. The precipitate was washed by decantation 4 times after which 1 liter of 15% NH_4OH was added, and stirred for 5 minutes, followed by dilution to 12 liters with distilled water. The washing by decantation was continued until peptization began. About 2 days were required for these operations in accordance with the requirements of Willstätter. The resulting precipitate was then washed with acetone and ether. Samples were dried, A_1 in vacuum, A_2 over P_2O_5 in vacuum, and A_3 at 110° in air.

X-Ray Examination. X-radiograms were made of the 6 samples above described. The position and relative intensities of the lines in the several samples are shown in Table VI and the diagrams for two of the samples only are reproduced in Fig. 7 (5 and 6). It is evident that all of Willstätter's samples formed by precipitation in the hot have the same crystal structure which is that of δ-Al_2O_3. The *D* sample obtained by rapid hydrolysis of aluminate in the cold gave an x-radiogram in which no lines could be detected.

TABLE VI

X-Ray Data for Willstätter's Preparations

A		B		D		New A_1		New A_2		New A_3	
D	I	D	I	D	I	D	I	D	I	D	I
3.16	7	3.15	5								
2.34	8	2.36	7					2.35	6		
1.85	10	1.85	10	General		1.85	10	1.85	10	1.85	10
		1.61	0.1								
1.43	8	1.43	8			1.43	7	1.43	7	1.43	8
1.31	6	1.32	6	Blackening				1.31	5		
1.13	2	1.13	1								

(3) *Ageing of Precipitated Alumina at 100°.*

Since a survey of reported work indicates that different products are obtained on ageing hydrous alumina in the hot and in the cold, the following systematic procedure was carried out: 200 g of $Al_2(SO_4)_3 \cdot 18H_2O$ was dissolved in 500 cc of water and 125 cc of 15 *N* NH_4OH was added with vigorous stirring. A sample containing the suspended oxide was removed at once and the remainder was heated to boiling under a reflux condenser. The boiling was continued several weeks, samples being removed from time to time and washed and dried according to the following procedure: Each sample was washed 7 times by the aid of the centrifuge with 50 cc portions of distilled water followed by 5 washings with 50 cc portions of acetone and then dried at 50°. No significance is attached to this particular procedure but it was followed with all samples so that the various compositions are comparable. Willstätter believes that washing with acetone removes all of the adsorbed water, leaving only chemically combined water. This appears to be definitely in error. However, in the present experiments washing with acetone was used as a convenient method of removing much of the water without the necessity of heating to a high temperature which might decompose definite hydrates, assuming they were present. After drying according to the above procedure the composition was determined and x-radiograms were made. The relationship between the age of sample and water content of the precipitate is given in Table VII and shown grapically in Fig. 8.

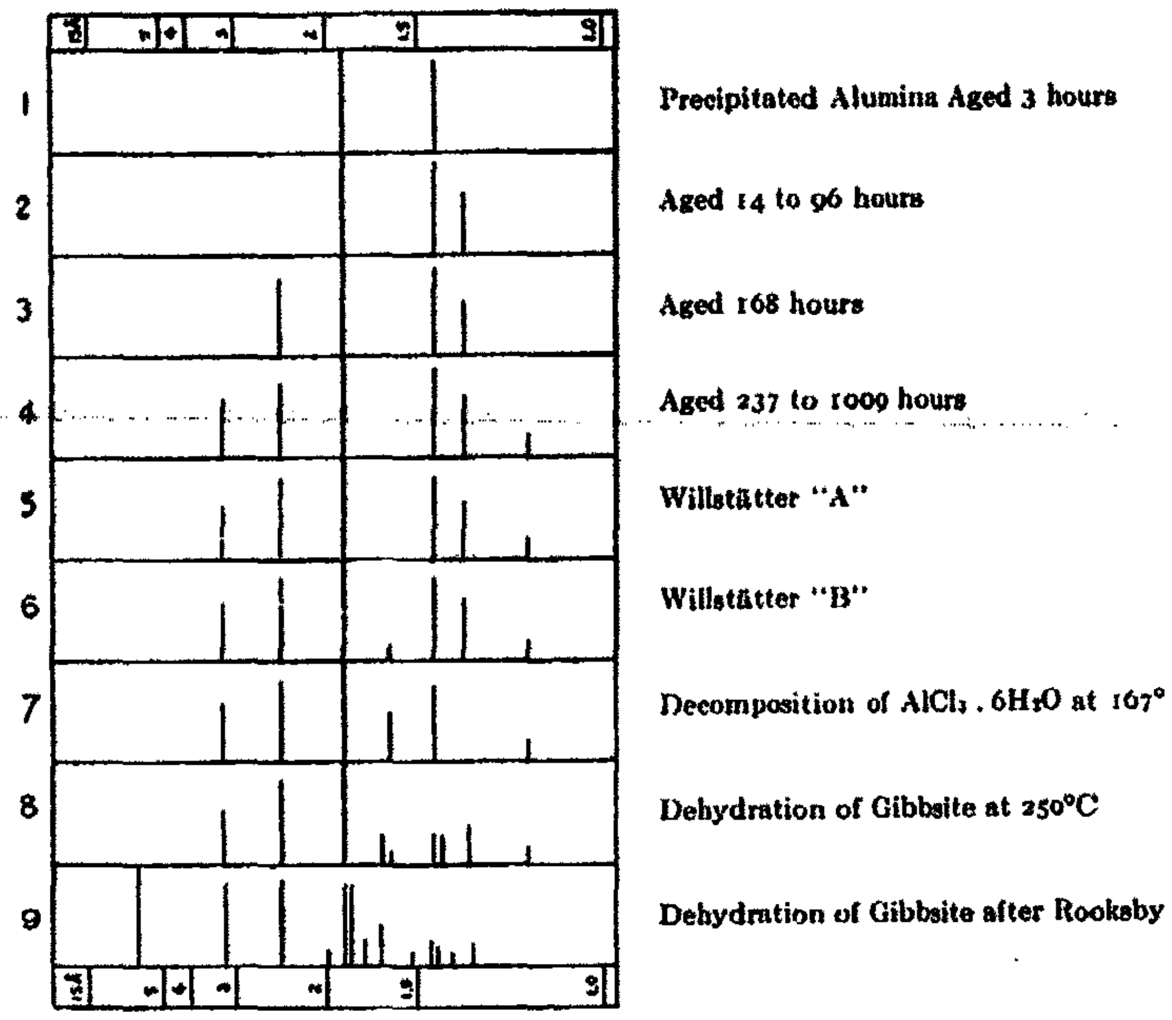

Fig. 7
X-Ray Diffraction Diagrams of Precipitated Aluminas prepared in Various Ways

TABLE VII

Age and Composition of Precipitated Alumina

Age hours	Composition % water	Numbers in Table 8	Numbers in Fig. 7	Age hours	Composition % water	Numbers in Table 8	Numbers in Fig. 7
0	74.73	1	–	96.5	24.15	7	2
1	—	2	–	168	—	8	3
3	40.89	3	1	237	22.51	9	–
14.5	—	4	2	335	—	10	–
24	34.65	5	2	504	—	11	–
72	26.88	6	2	1009	19.35	12	4

The x-ray diffraction data are given in Table VIII and Fig. 7. The results are quite conclusive. The precipitate is amorphous when first formed but ageing in the hot gradually causes a transformation to the crystalline form which shows the same lines on the x-radiogram as Willstätter's *A* and *B* samples.

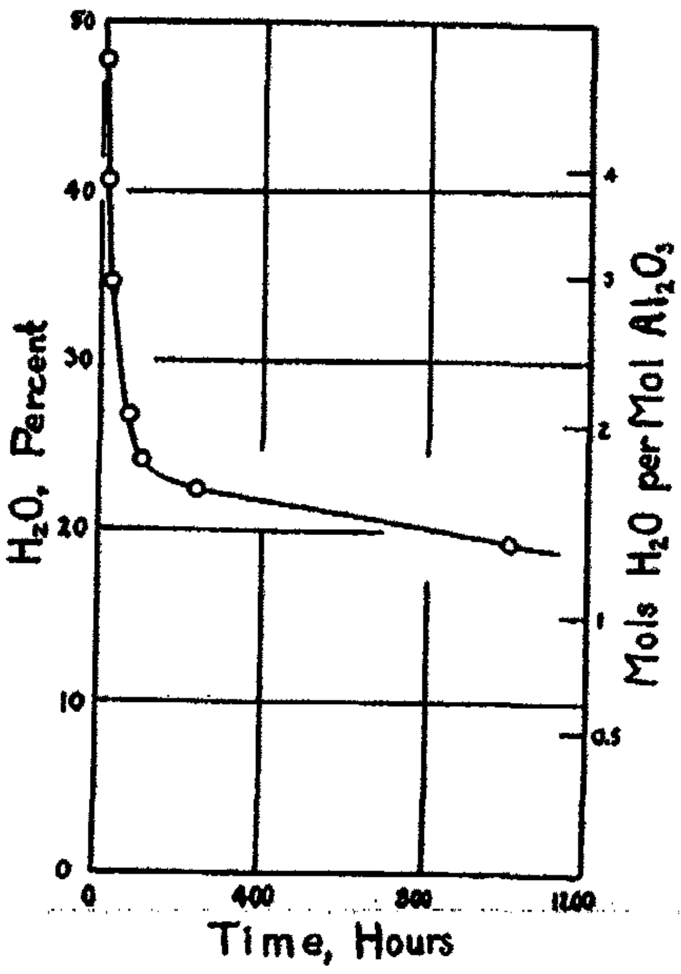

Fig. 8

Time-Composition Curve of Precipitated Alumina aged at 100°C.

Table VIII

X-Ray Diffraction Data for Alumin aged at 100°

1		2		3		4		5		6	
D	I	D	I	D	I	D	I	D	I	D	I
General blackening		General blackening		1.85	10	1.84	10	1.84	10	1.84	10
				1.43	10	1.43	9	1.43	9	1.43	9
						1.32	5	1.33	5	1.33	5

7		8		9		10		11		12 and 12a	
D	I	D	I	D	I	D	I	D	I	D	I
1.84	10	2.38	8	3.15	6	3.15	5	3.16	5	3.18	5
1.43	9	1.84	10	2.34	7	2.33	7	2.33	7	2.36	8
1.33	5	1.43	9	1.85	10	1.85	10	1.85	10	1.85	10
		1.33	5	1.43	9	1.435	8	1.43	8	1.43	8
				1.32	5	1.326	5	1.32	5	1.13	2
				1.14	2	1.14	2	1.13	1		

(4) Dehydration of Alumina aged at 100°.

Since all the samples described in the preceding paragraph were treated with acetone and dried at 50°, it was thought desirable to dry some of these at higher temperatures and thereby reduce the water content. Thus sample 12 having a composition 19.35% water when dried at 50° was heated for about 3 hours at 160° (sample 12a) at which temperature the composition became 10.38%, which corresponds to $Al_2O_3 \cdot 0.65H_2O$. X-ray examination showed that the crystal structure had not changed, the results for 12 and 12a being identical. It is obvious therefore that sample 12a, and therefore 12, cannot be diaspore or an isomer of diaspore ($Al_2O_3 \cdot H_2O$); but must be either a lower hydrate such as $Al_2O_3 \cdot 0.5H_2O$, or alumina with adsorbed water. In order to help decide this point, it is necessary to compare the x-radiogram from 12 with those obtained from anhydrous alumina.

Polymorphism of Alumina. δ-Al_2O_3. It has been demonstrated that four polymorphic forms of alumina exist: (1) α-Al_2O_3, which occurs in nature as corundum and has been prepared artificially by heating ordinary alumina to 1800°;[1] (2) β-Al_2O_3, prepared by allowing molten α-Al_2O_3 containing 0.5% MgO[2] or 5% Na_2O[3] to cool slowly; and (3) γ-Al_2O_3, formed by heating precipitated alumina in the neighborhood of 900°,[4] and (4) ζ-Al_2O_3 prepared by allowing molten α-Al_2O_3 containing 5% Li_2O to cool slowly.[5,6]

In 1928 Parravano and Montoro[7] reported the formation of another modification of alumina by heating $AlCl_3 \cdot 6H_2O$ for 15 days. Biltz, Lemke, and Meisel[8] called this alleged new modification δ-Al_2O_3. However in 1929 Parravano and Onorato[9] reported a serious error in the 1928 paper. "The spectrum reported in the work cited and attributed to be from alumina at 250° was due to an exchange of samples."

While Parravano's statement disposes of his δ-Al_2O_3, this does not mean that another polymorphic form does not exist. It will be recalled that precipitated alumina aged for many hours at 100°, gradually assumed a definite crystalline structure. Upon heating to 160° nearly all the water was driven off. It is most probable that this material is actually a polymorphic modification of Al_2O_3 which has been designated δ-Al_2O_3. Attempts were made to dry completely a sample of δ-Al_2O_3, but it was found that heating to higher temperatures starts the transformation to the γ-form, before the water is entirely driven off. It is probable that the last trace of water stabilizes the δ-form in somewhat the same manner as the β-form is stabilized by small amounts of Na_2O and MgO.

For purposes of comparison the x-ray diffraction patterns of the α, β, γ, δ, and ζ modification of alumina are given in chart form in Fig. 9. There can be no doubt that each of the five samples possesses a crystal structure entirely different from the others.

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[1] Davey: Phys. Rev., (2) **15**, 333 (1920); **21**, 716 (1923); Maugin: Compt. rend., **178**, 785 (1924); Pauling and Hendricks: J. Am. Chem. Soc., **47**, 781 (1925).

[2] Rankin and Merwin: J. Am. Chem. Soc., **38**, 568 (1916).

[3] Stillwell: J. Phys. Chem., **30**, 1444 (1926).

[4] Ulrich: Norsk. Geol. Tidsskr., **8**, 115 (1925); Hansen and Brownmiller: Am. J. Sci., (5) **5**, 225 (1928); Biltz; Lemke, and Meisel: Z. anorg. Chem., **186**, 373 (1930).

[5] Barlett: J. Am. Ceramic Soc., **15**, 361 (1932).

[6] The experiments of Barlett concerning ζ-Al_2O_3 have been repeated and the results confirmed.

[7] Atti. accad. Lincei, (6) **7**, 885 (1928).

[8] Z. anorg. Chem., **186**, 373 (1930) cf. Bragg, Gottfried, and West: Z. Krist., **77**, 255 (1931).

[9] Atti. accad. Lincei, (6) **10**, 475 (1929).

(5) *Thermal Decomposition of Aluminum Chloride.*

In view of the error in Parravano and Montero's report, experiments were carried out to determine, if possible, what form of alumina results on decomposing $AlCl_3 \cdot 6H_2O$. In the first experiment a 5 g sample of salt was placed in an electric oven at 150°. In 10 hours the temperature rose to 250° and the sample was maintained at this temperature for 2 hours. X-ray examination showed the resulting product to be amorphous. A second sample prepared by heating 17 hours at 225° and a third by heating at 250° for 30 days likewise proved to be amorphous. It was then decided to carry out the dehydration at a lower temperature since a higher temperature favors the transformation to γ-Al_2O_3. Accordingly, a sample was heated for 72 hours at 165-170°. This treatment was insufficient to decompose the hydrate completely; hence the sample was washed with hot water until nearly free from chloride and dried at 60°. X-ray examination showed that a crystalline product resulted which was identical with δ-Al_2O_3 as shown diagrammatically in Fig. 7 (7).

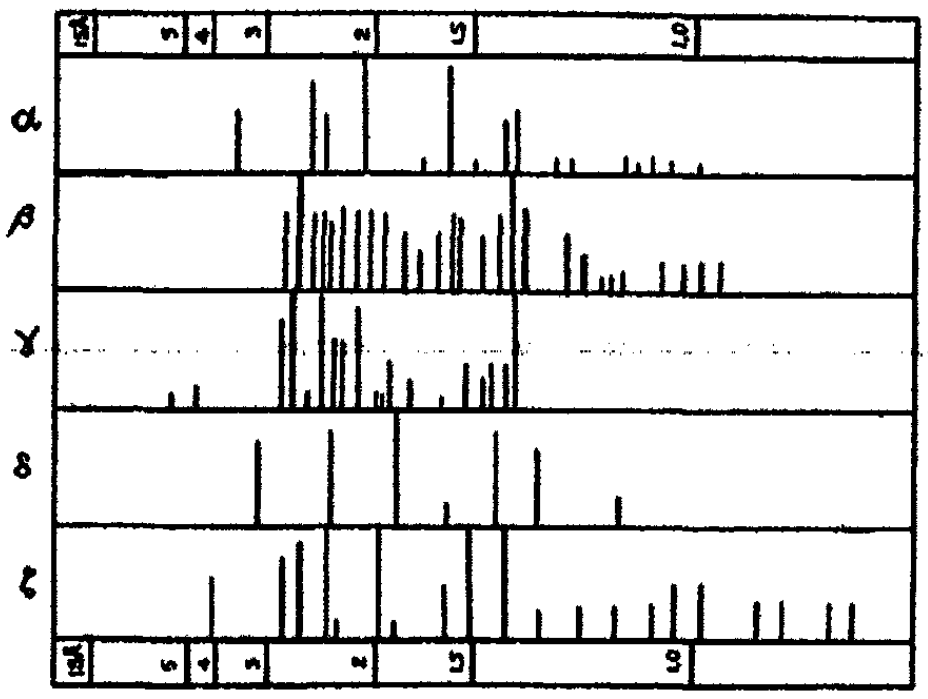


Fig. 9

X-Ray Diffraction Diagrams of α, B, γ, δ and $\zeta - Al_2O_3$

(6) *Thermal Decomposition of Gibbsite.*

Gibbsite, $Al_2O_3 \cdot 3H_2O$, starts to decompose on heating to a temperature in the neighborhood of 200°. (5) Rooksby obtained an x-radiogram of the product formed by thermal decomposition at a temperature of 250°. Under these conditions the composition of the product was represented by the formula $Al_2O_3 \cdot H_2O$. Since the x-radiogram is different from that of the mineral diaspore, Rooksby thought he had prepared an isomer of diaspore. On examination, the x-radiogram showed such a marked similarity to that of δ-Al_2O_3, that Rooksby's experiment was repeated. The x-radiogram is shown in Fig. 7 (8), together with those for δ-Al_2O_3 (1-7), and Rooksby's alleged hydrate (9). There is no doubt that the several preparations are identical in crystal structure.

(7) *Synthesis of Gibbsite.*

In the historical portion of this paper was included the diagram for the x-ray pattern of an artificial gibbsite which we prepared (Fig. 3, 12). The sample was made in the following way: To a solution of 56.1 g of KOH in 300 cc of water were added 10 g of Al strips, a little at a time to avoid frothing and heating. The resulting solution was filtered, placed in a stoppered flask, and allowed to stand. Upon examination about 30 days later, the bottom of the flask was covered with a micro-crystalline powder. This material was carefully washed, and dried at 60° and submitted to x-ray examination. The results obtained are given in Table IX and in Fig. 3 (12). For purposes of comparison the data for samples of the minerals "bauxite," gibbsite, and diaspore are likewise given in Table IX and Fig. 3 (10, 11, and 12).

The above method of synthesizing gibbsite is similar to that of Goudriaan. A sample prepared by Bonsdorff's method which is almost the same as Goudriaan's, gave an x-radiogram with the same spacings and intensities. It

TABLE IX

X-ray Data for Gibbsite and Diaspore

Number in Fig. 3

10 Gibbsite mineral		11 "Bauxite" mineral		12 Gibbsite artificial		13 Diaspore mineral	
D	I	D	I	D	I	D	I
4.85	10	4.85	10	4.85	10	4.00	10
4.34	9	4.34	9	4.36	8	2.57	8
3.31	1	3.31	1			2.34	10
3.12	1	3.12	1			2.13	10
2.45	7	2.45	7	2.45	6	2.08	2
2.38	7	2.38	7	2.38	6	1.82	1
2.26	1	2.26	1	2.26	3	1.71	2
2.17	3	2.17	3	2.17	3	1.63	10
2.04	3	2.04	3	2.04	3	1.54	1
1.990	2	1.990	2	1.985	3	1.50	2
1.907	2	1.907	2	1.911	3	1.47	2
1.798	3	1.798	3	1.795	3	1.40	8
1.741	4	1.741	4	1.741	3	1.38	1
1.681	5	1.681	5	1.680	4	1.34	1
1.642	0.1	1.642	0.1			1.32	1
1.580	1	1.580	1			1.29	1
1.448	4	1.448	4	1.448	4		
1.404	6	1.404	6	1.404	5		
1.352	2	1.352	2				
1.312	1	1.312	1				

will be recalled that Rooksby obtained different x-radiograms from samples made by those two methods and neither was identical with that of gibbsite. As already pointed out the reason for this is not obvious; but it is probable that he allowed the temperature to rise in the course of the preparation and so obtained δ-Al_2O_3 mixed with gibbsite in varying proportions.

Discussion of Results

From the experiments above described and from the earlier observations of Haber, Frick, and Weaver, and others, it is evident that alumina, freshly precipitated by the interaction of cold solutions of ammonia or alkali and a soluble aluminum salt, is either amorphous or contains such extremely minute crystals that it gives no x-ray diffraction pattern. When the gelatinous precipitate is allowed to age in the hot a crystalline phase appears which gives gradually, an x-ray diffraction pattern identical with that from aluminas obtained by the thermal decomposition of gibbsite, $Al_2O_3 \cdot 3H_2O$, at 250° and from the thermal decomposition of $AlCl_3 \cdot 6H_2O$ at 170°. Long continued ageing causes the crystals to grow as evidenced by the increase in number and sharpness of the lines on the x-ray pattern. Thus, by referring to Table VIII and Fig. 7 it will be seen that the gel aged for one hour gives a pattern showing only general scattering; but after three hours two rather broad bands appear. Continuing the process for several days finally results in a product which yields a pattern quite similar to the one resulting from the dehydration of gibbsite at 200-250°. As the material dehydrates no change is noted in the position of the lines showing that the gel is not a solid solution of alumina and water. The gel is therefore hydrous alumina, that is, alumina with adsorbed water, or a hydrous alumina hydrate.

According to Rooksby, the product formed by the thermal decomposition of gibbsite at 250° is $Al_2O_3 \cdot H_2O$ which gives a different x-radiogram from the mineral diaspore. Rooksby believes that the alleged hydrate from gibbsite is an isomer of diaspore. This conclusion is in error since the x-ray pattern of an aged precipitated alumina having the composition $Al_2O_3 \cdot 0.65H_2O$ is identical with that obtained with alumina from gibbsite. This pattern is different from the patterns obtained with α-Al_2O_3, β-Al_2O_3, γ-Al_2O_3, and ζ-Al_2O_3. It is concluded therefore that the product formed by (1) ageing precipitated alumina in the hot (b) decomposition of gibbsite at 250° and (c) decomposition of $AlCl_3 \cdot 6H_2O$ at 170° is a new polymorphic form of alumina which we have termed δ-Al_2O_3. The possibility that the so-called δ-Al_2O_3 is an alumina hemihydrate has not been definitely excluded but the evidence is against this point of view. In the first place, the data given in Table VII and Fig. 8 for the relation between composition and time of ageing at 100° shows that the precipitated gel loses water in the manner characteristic of hydrous oxides. In the next place, the vapor pressure-composition curve obtained by the precise measurements of Shidei (Fig. 1) gives no indication of the formation of alumina hemihydrate or of any other hydrate, in his preparation. Since his preparation was made by hot dialysis of precipitated alumina, he was working with a product formed by essentially the same procedure which we have found most favorable for the formation of δ-Al_2O_3. The obvious conclusion is that the product we have called δ-Al_2O_3 is not a hemihydrate.

The evidence from vapor pressure data and especially from x-ray diffraction data does not support the view of Hüttig and Willstätter that precipitated alumina can form a series of hydrates by ageing under suitable conditions. The various preparations of these authors are either δ-Al_2O_3 or a mixture of δ-Al_2O_3 and gibbsite. The formation of the former is favored by precipitation at high temperature and ageing at high temperature, while the formation of the latter is favored by precipitation and ageing in the cold. In any event the original precipitated gel is hydrous δ-Al_2O_3. Under favorable conditions the δ-Al_2O_3 first formed changes to gibbsite, the extent of the change being determined by the treatment of the sample.

Summary

The results of this investigation are as follows:

1. X-ray diffraction studies have been carried out on aluminas precipitated under widely varying conditions in order to determine what definite hydrates of alumina exist.

2. The evidence indicates that there are but two alumina hydrates: (1) gibbsite, $Al_2O_3 \cdot 3H_2O$, both natural and artificial, and (2) diaspore, $Al_2O_3 \cdot H_2O$.

3. Precipitated alumina aged at 100° has been found by x-ray diffraction methods to be a new form of alumina, which has been termed δ-Al_2O_3, with adsorbed water. It has not been prepared free from adsorbed water but a composition $Al_2O_3 \cdot 0.65H_2O$ has been obtained without transformation to the γ-Al_2O_3 taking place. The so-called δ-Al_2O_3 cannot be a monohydrate (Rooksby), but the possibility that it is a hemihydrate has not been definitely excluded, although the evidence is against this hypothesis.

4. Samples prepared according to the procedures of Hüttig and co-workers were found by x-ray diffraction methods to be either δ-Al_2O_3 or a mixture of δ-Al_2O_3 and gibbsite, instead of a series of definite hydrates as Hüttig believed.

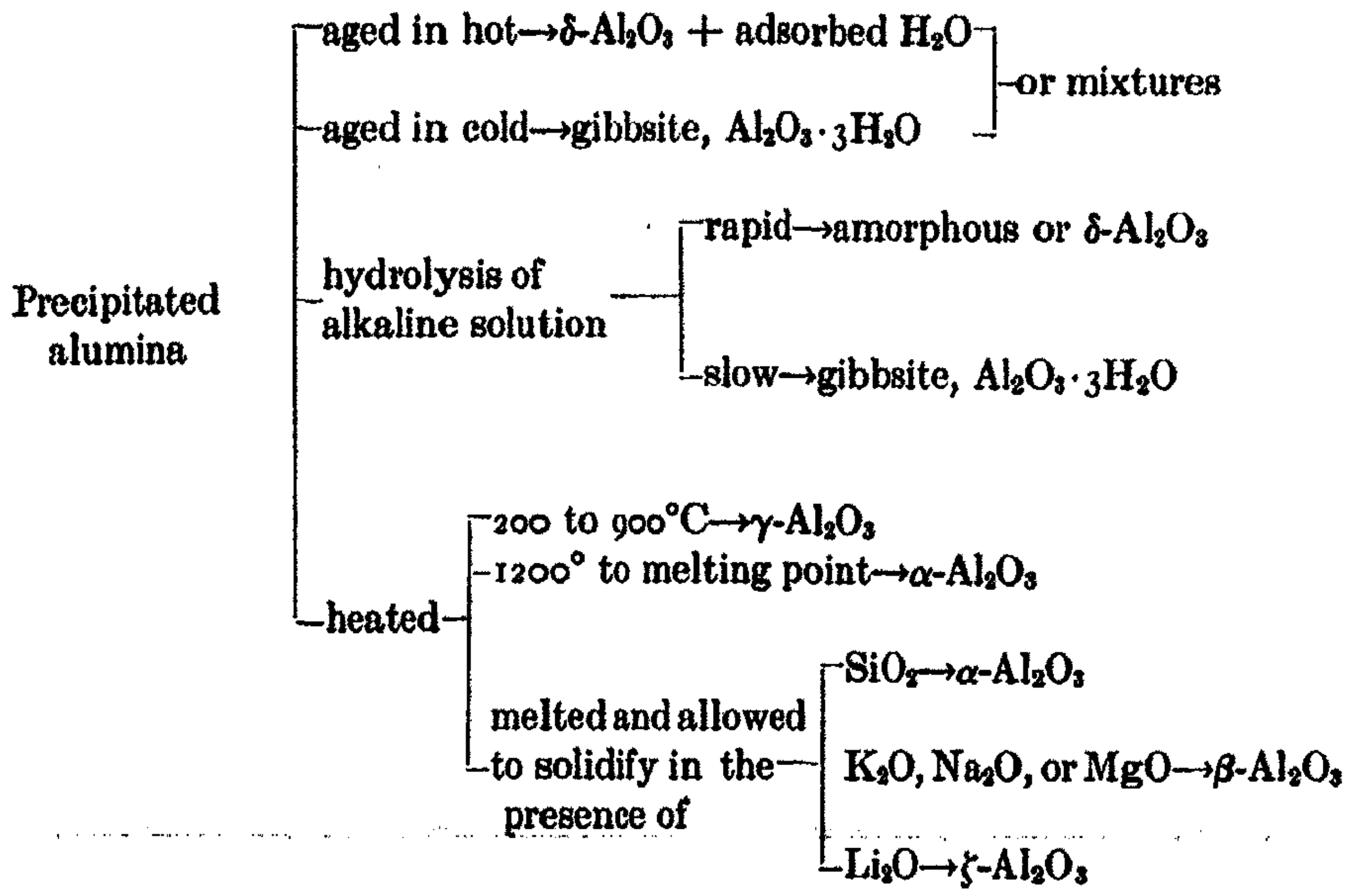
5. Samples prepared by the methods of Willstätter and co-workers were found by x-ray studies to be either δ-Al_2O_3 or amorphous Al_2O_3 with adsorbed water, instead of a series of hydrates as Willstätter believed.

6. Artificial gibbsites prepared by the methods of both Bonsdorff and Goudriaan give x-ray diffraction patterns identical with the mineral gibbsite.

7. The product formed by the thermal dehydration of gibbsite below 250°C is δ-Al_2O_3 and not an isomer of diaspore as Rooksby assumed. δ-Al_2O_3 is also formed by the thermal decomposition of $AlCl_3 \cdot 6H_2O$.

8. The existence of ζ-Al_2O_3 recently announced by Barlett, has been confirmed.

9. The various transformations of precipitated alumina may be tabulated in the following diagram:



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X-RAY STUDIES ON THE HYDROUS OXIDES

II. Stannic Oxide

BY HARRY B. WEISER AND W. O. MILLIGAN

The question of the so-called stannic acids and the existence of definite hydrates of stannic oxide have been the subject of repeated investigations from the time of Berzelius to the present. The colloidal nature of the so-called stannic acids was investigated by van Bemmelen,[1] and by Mecklenburg[2] who concluded that the α and β acids were both hydrous oxides differing from each other in the size of the particles. This same conclusion was reached by one of us[3] ten years ago. Investigations made at that time showed that there was no definite dividing line between the two preparations, and that the β oxide consisted of the larger particles. Gutbier, Hüttig, and Döbling[4] concluded from pressure-temperature curves that no definite hydrates[5] were formed. The x-ray diffraction patterns of their various samples as well as those of Mecklenburg which had aged for several years, showed that the original hydrous oxide was apparently amorphous and that the aged products exhibited a gradual formation of a crystal lattice identical with the mineral cassiterite, SnO_2. X-radiograms made by Yamada[6] of several different preparations,[7] all revealed a structure identical with the anhydrous stannic oxide. Further x-radiograms of the so-called α and β stannic acids were made by Posnjak[8] who demonstrated clearly that the structure of both is identical with the anhydrous oxide; and that the difference in the two oxides is due to a difference in particle size, the β being the larger. This is in accordance with the observations of Mecklenburg and of Weiser. Hydrous SnO_2 was dried in a vacuum over P_2O_5 by Forster[9] who concluded from x-ray data that the products obtained had the structure of cassiterite. X-radiograms of the fresh gel and the products resulting from the ageing and heating of colloidal SnO_2 were obtained by Böhm.[10] His published photographs show clearly the gradual increase in particle size from the original hydrous oxide to the anhydrous SnO_2, the lattice in all cases remaining identical with that of cassiterite.

In view of all the apparently conclusive evidence that is available, it would appear that the question of the nature of the so-called stannic acids should be

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[1] "Die Absorption," 54 (1910).

[2] Z. anorg. Chem., **74**, 207 (1912).

[3] Weiser: J. Phys. Chem., **26**, 654 (1922).

[4] Ber., **59**, 1232 (1926).

[5] Cf., however, Willstätter and Kraut: Ber., **59**, 2541 (1926).

[6] J. Chem. Soc. Japan, **44**, 210 (1923).

[7] Rose: Pogg. Ann., **75**, 1 (1848); Engel: Ann. Chim. Phys., (3) **12**, 463 (1844); Graham: Pogg. Ann., **123**, 538 (1864); Schneider: Z. anorg. Chem., **5**, 82 (1894); Zsigmondy: Ann., **301**, 361 (1898); Collins and Wood: J. Chem. Soc., **121**, 441 (1922).

[8] J. Phys. Chem., **30**, 1073 (1926).

[9] Physik. Z., **28**, 151 (1927).

[10] Kolloid-Z., **42**, 283 (1927).

considered a settled one; but such is not the case. In a recent investigation Thiessen and Koerner[1] claim that a stannic oxide gel prepared by the slow hydrolysis of stannic ethylate gives pressure-temperature and composition-temperature curves that indicate the formation of a series of hydrates. From pressure-composition data the following hydrates are claimed: $2SnO_2 \cdot 5H_2O$; $SnO_2 \cdot 2H_2O$, $4SnO_2 \cdot 7H_2O$ and $2SnO_2 \cdot 3H_2O$ and from temperature-composition curves; $SnO_2 \cdot H_2O$ and $2SnO_2 \cdot H_2O$. X-radiograms of the several preparations were made, but no definite results were obtainable by this method. It was claimed that the lattice undergoes a slight expansion as the water content decreases;[2] but that the "strong diffuse blackening" of the film renders impossible the making of exact measurements.

Experimental

In view of the theoretical significance of the existence or non-existence of a series of SnO_2 hydrates, it is the purpose of the present paper to consider (1) the dehydration of stannic oxides at temperatures which are said to give definite hydrates; and (2) the examination of these reputed hydrates by x-ray diffraction methods.

I. The Thermal Dehydration of Hydrous Stannic Oxide.

A. Stannic Oxide prepared by Thiessen and Koerner's Method

Preparation of Oxide. The stannic oxide was prepared according to the procedure outlined in detail by Thiessen and Koerner. Sodium ethylate made by adding metallic sodium to absolute alcohol was allowed to react with an anhydrous $SnCl_4$ solution in absolute alcohol in accord with the following equation: $SnCl_4 + 4NaOC_2H_5 \rightarrow Sn(OC_2H_5)_4 + 4NaCl$. All reactions were carried out with extra precautions to prevent the entrance of water vapor into the apparatus or solutions. The resulting mixture of stannic ethylate and NaCl was digested on a water bath, and finally the NaCl was filtered off. An amount of the alcoholic solution of ethylate equivalent to 25 g of anhydrous SnO_2 was added to 5 liters of absolute alcohol. The resulting solution was allowed to stand with occasional stirring in a flask with a neck 5 cm in diameter. Moisture from the air hydrolyzed the stannic ethylate, the process being complete in 26 days. The gelatinous precipitate of SnO_2 was filtered off, washed with 1 liter of 96% alcohol in 100 cc portions, dried with suction on a filter paper, and kept in a glass-stoppered bottle until used.

Rate of Dehydration. The SnO_2 gel made by the above method consists of SnO_2 alcohol, and water. Thiessen and Koerner obtained a composition-temperature curve by heating a sample at definite temperatures for 15 minutes over $CaCl_2$. The resulting curve is shown in Fig. 1. The breaks in the curve are indicative of the formation of the definite hydrates $SnO_2 \cdot H_2O$ and $2SnO_2 \cdot H_2O$.

It would not be expected that an equilibrium state would result from heating the samples for only 15 minutes, and Thiessen and Koerner give no data to

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[1] Z. anorg. Chem., 195, 83 (1931).

[2] Cf. Forster: Physik. Z., 28, 151 (1927).

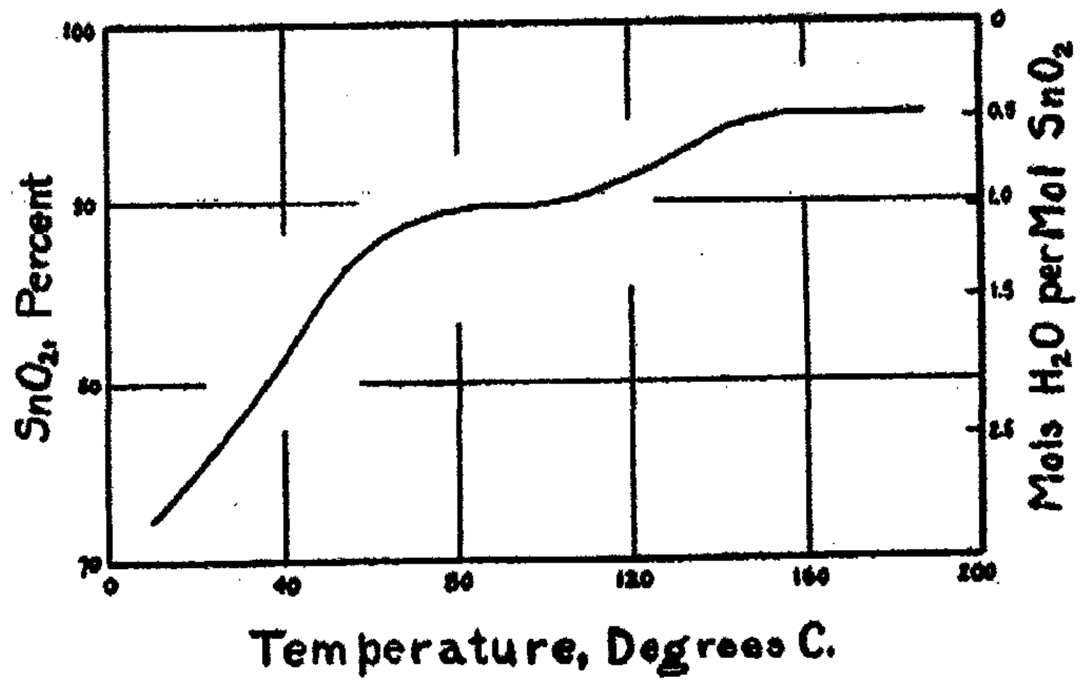

FIG. 1
Temperature-Composition Curve of Stannic Oxide (after Thiessen and Koerner)

show whether or not this is the case. It was thought desirable to determine the time required for equilibrium at a given temperature before proceeding to obtain the composition-temperature curve. To do this a sample was placed in an electric oven with the temperature adjusted to 50°C. The sample was removed at intervals, allowed to cool, weighed, and the heating continued. The resulting curve showing the relation between composition and time of heating, is given in Fig. 2. It will be observed that about 8 hours is required to attain equilibrium at the temperature stated. As would be expected, equilibrium is established more rapidly at higher temperatures; thus at 160°, 2 or 3 hours is sufficient.

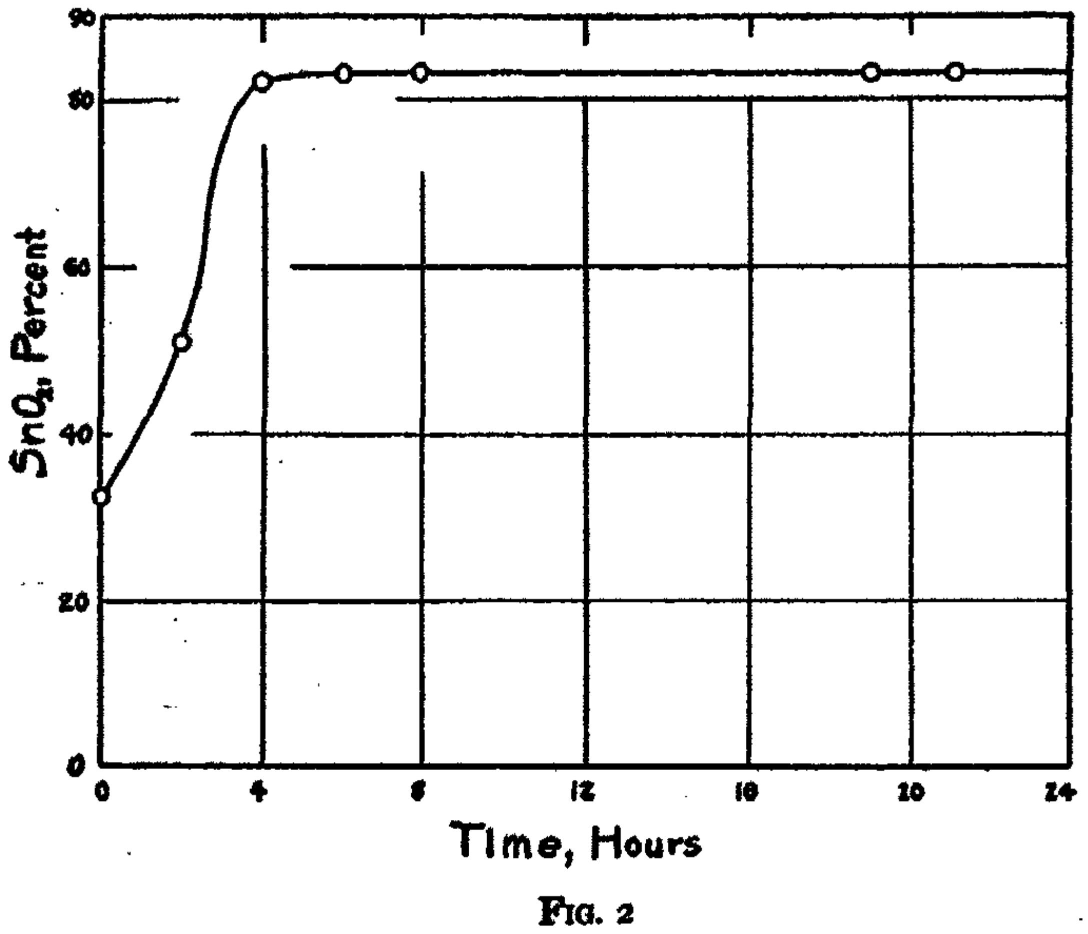

FIG. 2
Rate of Dehydration of Stannic Oxide at 50°C

The form of the time-composition curve is what would be expected from a material containing water and a little alcohol: the rate of drying is quite rapid at first and then falls off, decreasing to a relatively low value before the composition becomes constant. This means that, at first, alcohol and some of the water comes off followed by the greater portion of the water leaving the last trace of water which, as is well known, is very difficult to remove.

The Composition-Temperature Curve. In the light of the above experiments a composition-temperature curve was obtained, taking care to heat the sample at each temperature for at least 12 hours to ensure the establishment of equilibrium. Two samples were taken: the first was allowed to cake into a lump as the heating proceeded, and the second was pre-dried enough to allow it to be powdered. The samples were placed in weighing bottles, and heated to constant weight over calcium chloride at a definite temperature, after which the temperature was raised and the heating continued as before. The dehydration was carried out in a thermo-regulated electric oven, the temperature of

TABLE I

The Thermal Dehydration of Thiessen and Koerner's SnO_2

Temperature °C	Not powdered		Powdered	
	Weight of sample g	SnO_2 %	Weight of Sample g	SnO_2 %
39.6	0.9073	83.25		
40.6	0.9069	83.29		
48.4	0.8997	83.95		
56.3	0.8933	84.56		
60.2	0.8899	84.88		
63.6	0.8857	85.28		
67.8	0.8753	86.29	0.3996	86.13
69.8	0.8735	86.47	0.3989	86.28
74.5	0.8707	86.75	0.3971	86.67
78.6	0.8690	86.92	0.3964	86.82
81.6	0.8674	87.08	0.3953	87.06
85.7	0.8671	87.11	0.3950	87.13
90.0	0.8654	87.28	0.3943	87.29
95.4	0.8637	87.45	0.3935	87.46
100.4	0.8598	87.85	0.3916	87.89
104.7	0.8575	88.09	0.3908	88.07
110.0	0.8549	88.35	0.3894	88.38
116.0	0.8540	88.45	0.3889	88.50
120.0	0.8536	88.49	0.3888	88.52
123.5	0.8531	88.54	0.3887	88.54
132.3	0.8510	88.76	0.3870	88.93
143.2	0.8465	89.23	0.3847	89.46
154.0	0.8423	89.68	0.3833	89.79
202.0	0.8283	91.19	0.3780	91.05

which remained constant within 0.5°. For temperatures below 100° a thermometer was used that had been calibrated against a standard thermometer checked by the Bureau of Standards. Above 100° an accurate thermometer was employed which had been checked at points below 100° against the standard thermometer. The results obtained are given in Table I and in Fig. 3.

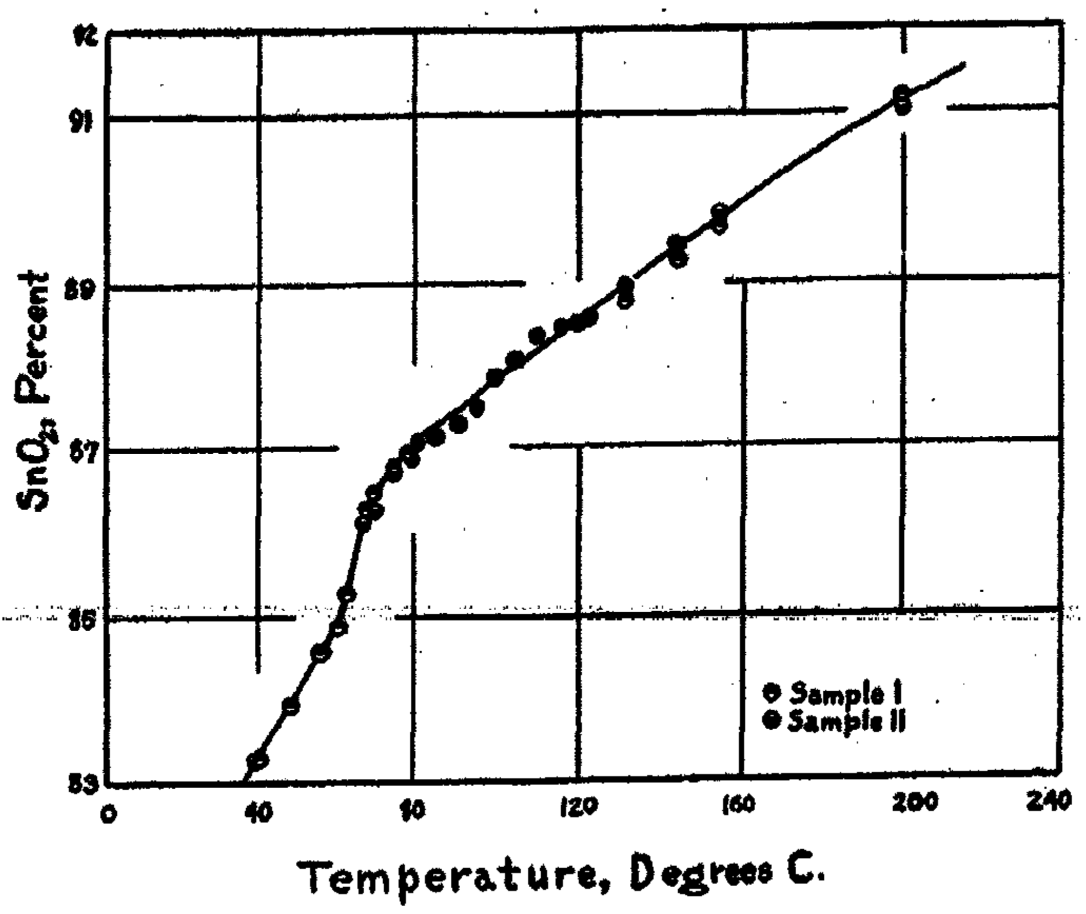

Fig. 3

Temperature-Composition Curve of Stannic Oxide prepared by Hydrolysis of Stannic Ethylate

B. Alpha and Beta Stannic Oxides

For purposes of comparison dehydration curves were obtained for samples of the so-called α and β stannic oxides. A sample of α oxide was prepared by the addition of a slight excess of ammonium hydroxide to a solution of $SnCl_4$. The resulting gelatinous precipitate was washed by centrifuging, and finally

Table II

The Thermal Dehydration of Alpha and Beta SnO_2

	Alpha		Beta	
Temperature °C	Weight of sample g	Loss in weight %	Weight of sample g	Loss in weight %
39.6	1.8620	0.0	3.7966	0.0
49.0	1.7980	4.33	3.7395	1.50
59.4	1.7267	7.27	3.6398	4.13
69.1	1.6944	8.95	3.5863	5.54
80.3	1.6698	10.32	3.5422	6.70
89.6	1.6511	11.33	3.5166	7.38
99.6	1.6317	12.42	3.4938	7.98

air-dried until it could be powdered. The β oxide was prepared by treating pure metallic tin with concentrated HNO_3, washing and drying the resulting product in the air. The dehydration of both samples was carried out according to the procedure given above. The results are given in Table II and in Fig. 4. The percentage loss in weight of Thiessen and Koerner's stannic oxide was calculated at each temperature and the results shown in the third curve of Fig. 4.

The significance of the curves obtained from the various preparations will be discussed after a consideration of the results found by an x-ray examination of the alleged hydrates of Thiessen and Koerner.

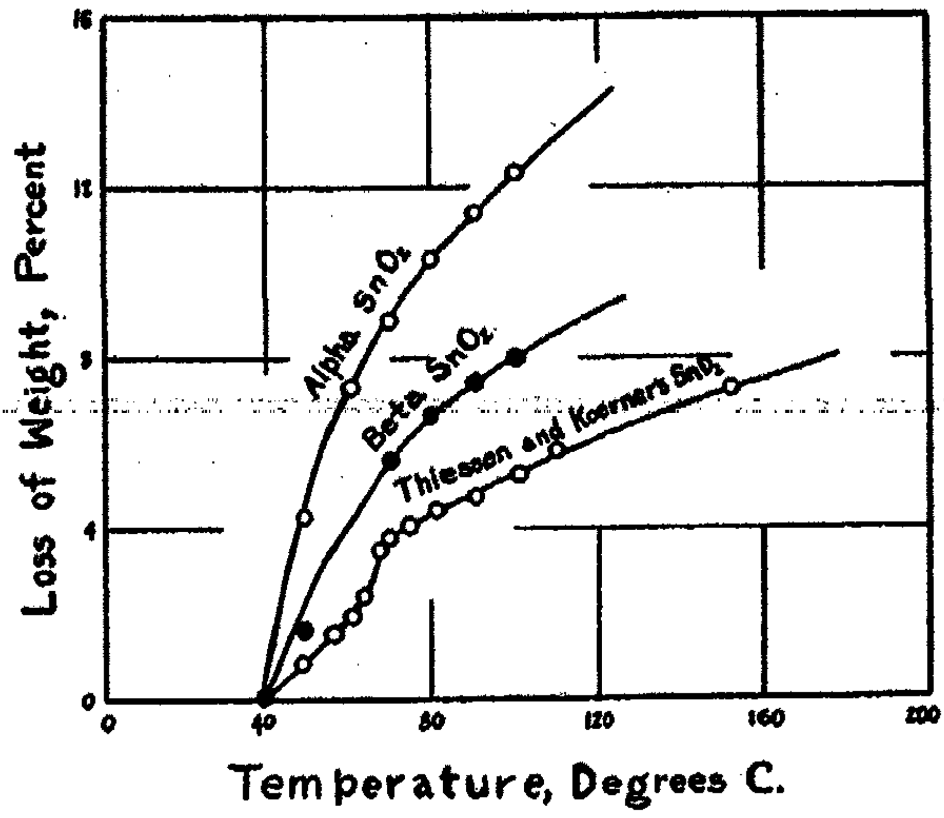

FIG. 4

Temperature-Composition Curves of the So-called Alpha and Beta Stannic Oxides

II. *X-Ray Examination of Thiessen and Koerner's Stannic Oxide.*

Separate samples of SnO_2 prepared by the method of Thiessen and Koerner were heated to temperatures that should give definite hydrates according to the composition-pressure and composition-temperature curves of these investi-

TABLE III

X-Ray Diffraction Data for Dehydrated SnO_2

1 25°		2 36°		3 50°		4 90°		5 160°		6 Cassiterite	
D	I	D	I	D	I	D	I	D	I	D	I
3.35	10	3.37	8	3.40	8	3.35	8	3.35	9	3.40	10
2.65	10	2.65	10	2.64	10	2.63	10	2.65	10	2.67	10
										2.35	5
1.78	10	1.78	10	1.77	10	1.78	10	1.77	10	1.77	10
1.43	5	1.44	5	1.43	5	1.43	4	1.44	5	1.43	7
										1.32	2
										1.21	5
										1.16	2
										1.10	4
										1.05	1

gators. The following temperatures were chosen: 25°, 36°, 50°, 90°, and 160°. Specimens of the heated samples were sealed in tubes of "nonex" glass (a special glass made of materials of low atomic weight) and x-radiograms made by the powder method in the usual manner, using a General Electric x-ray diffraction apparatus. In each case the pattern of NaCl was obtained on the same film for purposes of calibration. The interplanar spacings and the visually estimated relative intensities are given in Table III and in chart form in Fig. 5. The spacings are in Ångstrom units and the intensities on such a scale that the most intense line is designated as 10.

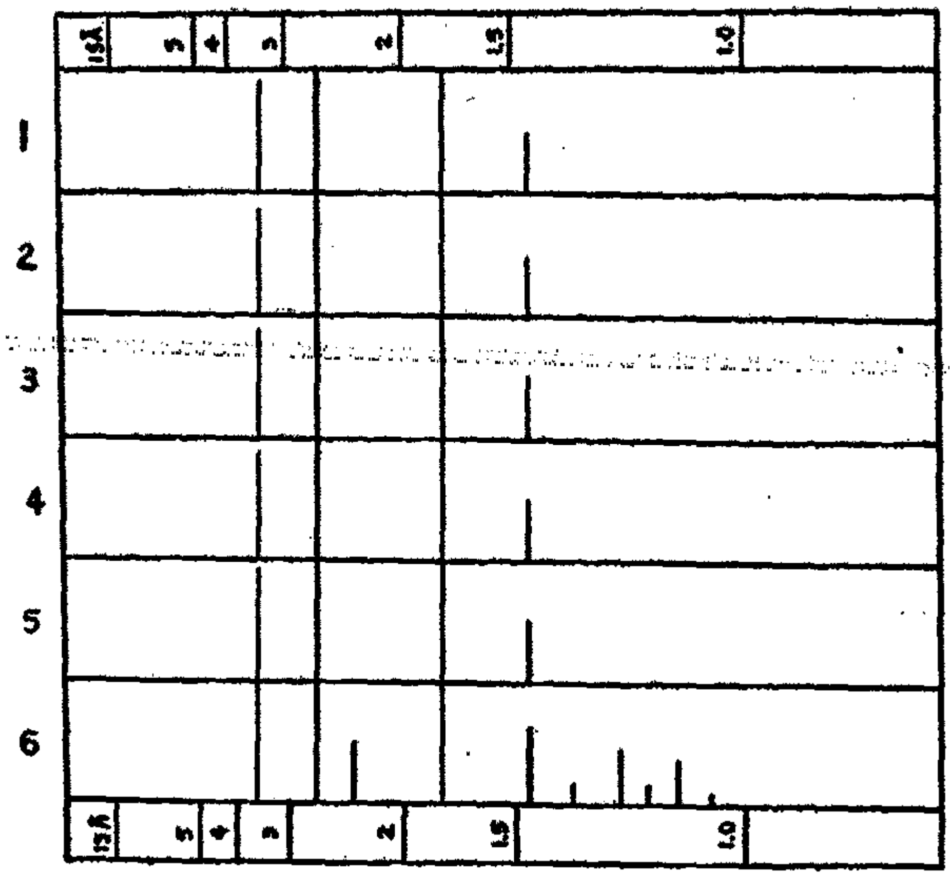

Fig. 5

X-Ray Diffraction Patterns for Stannic Oxides: Thiessen and Koerner's Preparations dehydrated at (1) 25°C, (2) 36°C, (3) 50°C, (4) 90°C, and (5) 160°C, (6) The Mineral SnO_2.

Discussion of Results

Composition-temperature curves of hydrous stannic oxide have previously been obtained by Carnelley and Walker[1] and by van Bemmelen.[2] The smooth curves obtained by these investigators were quite similar to those for the α and β stannic oxides, shown in Fig. 4. The curve obtained from the preparation of Thiessen and Koerner is similar except for a change in its direction at about 60–70°. The reason for this is obvious when it is recalled that the material consists of SnO_2, water, and a little alcohol. The odor of alcohol is still apparent in a sample that has been heated to 40° and there is no question but that traces of alcohol persist at least up to the boiling point. As has been seen, samples of SnO_2 containing only water give a smooth, continuous curve. Samples containing alcohol but no water would be expected to give a curve of

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[1] J. Chem. Soc., 53, 83 (1888).

[2] "Die Absorption," 54 (1910).

the same type but would reach the maximum sooner. In the case under consideration, in which both loss of alcohol and loss of water are superimposed on the same curve, the two effects added together algebraically would be expected to give a curve of the shape found experimentally to hold. Since Thiessen and Koerner did not allow sufficient time for equilibrium to be established, the breaks in their curves are without significance so far as hydrate formation is concerned. This point has already been adequately discussed by Posnjak in connection with similar results of Willstätter and Kraut.

Since the crystal structure of all the products formed at various temperatures is identical with the mineral cassiterite, SnO_2, with respect to the position and relative intensity of the lines on the x-radiograms, no definite hydrates of SnO_2 are actually formed. The only difference in the diffraction effects is that the size of the particle, as indicated by the width of the lines in the products obtained by dehydration, are smaller than those which compose the mineral cassiterite. It should be noted from Table III and Fig. 5, that the interplanar spacings do not change (within the expected experimental error for such wide lines) with varying amounts of water, as would be the case if the SnO_2 and water formed a solid solution. This shows that the water must be adsorbed on the surface of the finely-divided crystals.

Hydrous SnO_2, whether in the so-called α or β form or as prepared by the method of Thiessen, consists of very small crystals of SnO_2 which adsorb water or both water and alcohol in the Thiessen preparation. When the latter material is dehydrated, at temperatures up to about 60–70° most of the alcohol and some of the water is driven off; at temperatures above this point where little alcohol is left, the dehydration proceeds in a uniform manner as in the case of the familiar α and β preparations.

Thiessen and Koerner found that the general blackening of the film upon which the x-ray diffraction patterns were recorded precluded accurate measurements, and concluded that the method was not suitable for distinguishing the presence or absence of hydrate formation. No such difficulties are encountered, however, when the proper exposure is made, and a special glass of low atomic weight is used. It is true, of course, that the broad, diffuse lines cannot be read with the accuracy obtainable on sharper lines; nevertheless all lines recorded in Table III are clearly visible on the original negatives.

Summary

The results of this investigation are as follows:

1. Hydrous stannic oxide has been prepared by the hydrolysis of stannic ethylate according to the method of Thiessen and Koerner, who claim that a series of definite hydrates of SnO_2 results from the thermal dehydration of this material.

2. Composition-temperature curves have been obtained under conditions that ensure the establishment of equilibrium. The curves are smooth indicating the absence of hydrate formation. Breaks in the curves of Thiessen and

Koerner were due to their failure to allow sufficient time for equilibrium to be established under a given set of conditions.

3. X-radiograms of preparations obtained by dehydration at definite temperatures, show that no definite hydrates are actually formed, the several products consisting of SnO_2 of varying particle size with varying amounts of adsorbed water. This confirms the observations of Gutbier, Hüttig, and Döbling; Posnjak; Yamada; Weiser; and others.

4. The claim of Thiessen and Koerner, that the x-ray diffraction method is not suitable for determining the presence or absence of hydrates, has been shown not to be valid; on the contrary, when the proper precautions are taken the results are definite and conclusive.

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X-RAY STUDIES ON THE HYDROUS OXIDES
III. Stannous Oxide

BY HARRY B. WEISER AND W. O. MILLIGAN

Historical

Anhydrous Stannous Oxide. Stannous oxide was prepared by Berzelius[1], by the addition of K_2CO_3 in excess to a solution of stannous salt. Gay Lussac[2] obtained a hydrous precipitate with NH_4OH, and dehydrated this material by boiling under water until a black SnO appeared. Ditte[3] stated that the presence of NH_4OH prevented the alleged transformation to the anhydrous oxide; however if the NH_3 is boiled off, the dehydration proceeds. An excess of alkali, insufficient to dissolve the oxide, favors the transformation.[4] Sandall[5] prepared a black form of SnO by grinding fused $SnCl_2$ with $Na_2CO_3 \cdot 10H_2O$. The blue-black oxide of Berzelius became brownish-green when pounded or ground. Upon heating, an olive-green color developed.[6] Frémy evaporated a dilute solution of NH_4Cl in which precipitated SnO was suspended; when crystals of NH_4Cl appeared, the hydrous material was said to change to a cinnabar-colored powder which was transformed to greenish-brown upon rubbing with a hard body. Roth[7] obtained a red oxide by digesting the hydrous material with CH_3COOH; but Bury and Partington[8] were unable to prepare this form. Frankel and Snipischsky[9] added NaOH to a solution of $SnCl_2$; the white precipitate was transformed into a blue powder when boiled for several hours on a bath of saturated NaCl solution. Frémy believed that three modifications of SnO exist, namely: (1) the blue-black, crystalline oxide made by digesting hydrated SnO with excess alkali, (2) the olive-green powder obtained by heating the black modification, and (3) the cinnabar-colored powder resulting from the slow evaporation of a suspension of precipitated SnO in a dilute NH_4Cl solution.

Precipitated Stannous Oxide. The precipitate obtained by the interaction of solutions of stannous salts and an alkali has been formulated $Sn(OH)_2$, although there is no evidence that such is the case. Proust[10] found that an excess of K_2CO_3 gave a white precipitate containing 5% water. Schaffner[11] believed

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[1] Gilbert's Ann., 42, 284 (1812); Pogg. Ann., 28, 443 (1833); Ann. Chim. Phys., (1) 87, 50 (1813); (2) 5, 149 (1817).

[2] Ann. Chim. Phys., (2) 1, 40 (1816).

[3] Ann. Chim. Phys., (5) 27, 145 (1882); Compt. rend., 94, 792, 864 (1882).

[4] Nordenskjöld: Pogg. Ann., 114, 612 (1861).

[5] Phil. Mag., (3) 12, 216 (1838).

[6] Frémy: Ann. Chim. Phys., (3) 12, 460 (1844); 23, 385 (1848).

[7] Ann., 60, 214 (1846).

[8] J. Chem. Soc., 121, 1998 (1922).

[9] Z. anorg. Chem., 125, 235 (1922).

[10] J. phys., 51, 173 (1800); 61, 338 (1804); Ann. Chim. Phys., (1) 28, 213 (1798); Nicholson's J., (1) 2, 515 (1798); (2) 14, 38 (1806).

[11] Ann., 51, 174 (1844).

that NH_4OH gave a basic salt. K_2CO_3 was said to give a precipitate that had the composition $2SnO \cdot H_2O$ when dried below 80°C.

TABLE I

Precipitated from $SnCl_2$ by	Color	Dried	Composition % water
NaOH	Yellow tinge	Vacuum, P_2O_5, 14 da	7.11
Na_2CO_3	Yellow tinge	$CaCl_2 + P_2O_5 + KOH$, 14 da	8.54
NH_4OH	Yellow, dried	P_2O_5	8.32
NH_4OH (CO_2 atmosphere)	Yellow, dried	P_2O_5	8.82
Na_2CO_3 (CO_2 atmosphere)	Yellow tinge	Vacuum, P_2O_5, 14 da	7.4
NaOH + Na_2CO_3	—	110°C air bath	2.5

Ten years ago Bury and Partington[1] investigated the hydrous precipitate prepared in several ways; the various methods used are listed herein as Table I. These investigators concluded that all samples were the same except the last, and that the composition was $3SnO \cdot 2H_2O$. It was observed,[2] that when precipitated SnO stood in a glass vessel, the portion in contact with the glass darkened. Bury and Partington attributed this to the action of traces of alkali on the surface of the glass, since it is well known that excess alkali favors the transformation to the blue-black oxide. This view was apparently substantiated by the observation that samples kept in silica tubes did not blacken.

Brown and Henke[3] treated $SnCl_2$ solution in a glass cylinder with Na_2CO_3. The first preparation was white when precipitated and slightly yellow when dried. Subsequent precipitates darkened before washing was complete. The blackening was said to begin along the sides of the glass cylinder in streaks coincident with scratches on the glass caused by a stirring rod. Washing with concentrated HCl had no effect, but treatment with NaOH prevented further blackening of the precipitate. Brown and Henke believed that the first black particles act as catalysts to produce further blackening, but offer no explanation as to the formation of the initial particles. The theory of Bury and Partington would have predicted that treatment with alkali would produce more rather than less blackening. It is probable that some other factor is entering in. This is suggested by Roth's observation that one of his preparations rapidly turned black upon exposure to sunlight.

The present investigation includes (1) an examination of the various modifications of SnO by x-ray diffraction methods in order to determine whether the differences in color and other properties are due to the existence of polymorphic forms of SnO, to varying particle size, or to some combination of these effects; (2) a study of precipitated SnO to find out whether it is a hydrous oxide or a hydrous hydrate; and to determine the conditions that effect the blackening.

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[1] J. Chem. Soc., **121**, 1998 (1922).

[2] Cf. Ditte: Loc. cit.

[3] J. Phys. Chem., **27**, 739 (1923).

Experimental

Anhydrous Stannous Oxide.

A. Blue-black α-SnO. A solution of 25 g of $SnCl_2 \cdot 2H_2O$ in 200 cc of water was cleared up with HCl and 20 g of NaOH in 200 cc of water was added. A white or faintly yellow precipitate formed which turned to a blue-black powder upon heating to boiling. This powder was washed thoroughly by decantation and was dried for 18 hours at 110°C.

B. Brownish-green α-SnO. A portion of *A* was ground in an agate mortar; this treatment gave a brownish-green powder.

C. Greyish-green β-SnO. Another portion of *A* was heated in a vacuum in a pyrex tube. At about 550°C the blue-black crystals were transformed to a greyish-green powder.

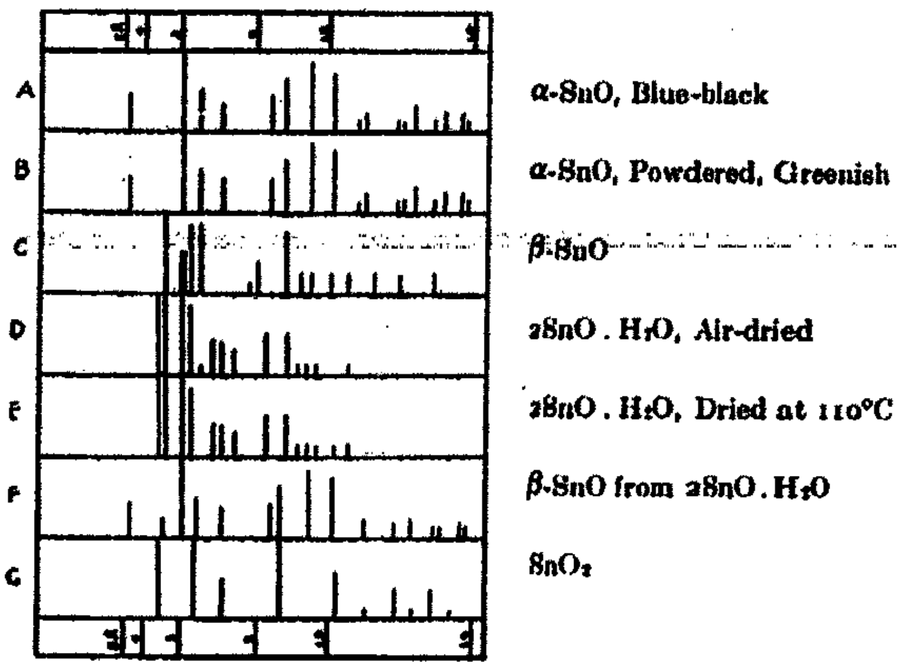

FIG. 1

X-Ray Diffraction Diagrams of Stannous Oxides and Stannous Oxide Hemihydrate

Attempts to prepare the red forms of Roth and of Frémy were unsuccessful, in confirmation of the results of Bury and Partington.

Samples of each of the above described preparations were sealed in nonex glass tubes, and x-ray diffraction photographs were obtained using the General Electric X-Ray Diffraction Apparatus. Pure NaCl was used to calibrate the film. The results are given in Table II and Fig. 1. The interplanar spacings $D = d_{hkl}/n$ are expressed in Ångstrom units; and the relative, estimated intensities, I, are expressed on such a scale that 10 means the most intense line on a given film. The pattern obtained from the α-SnO corresponds to a tetragonal structure of the PbO type[1] with $a_0 = 3.78$ Å and $c_0 = 4.79$ Å. The calculated density is 6.51. The results are almost identical with the values found by Levi,[2] who obtained $a_0 = 3.77$ Å and $c_0 = 4.77$ Å. The pattern of β-SnO was not studied further. The results indicate that SnO exists in two polymorphic

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[1] Dickinson and Friauf: J. Am. Chem. Soc., **46**, 2457 (1924).

[2] Nuovo Cimento, (8) **1**, 335 (1924); **3**, 114 (1926); cf. Wyckoff: "The Structure of Crystals," 228 (1931).

TABLE II

X-Ray Diffraction Data for Anhydrous and Hydrated SnO

Sample									
A & B α-SnO		C β-SnO		D $2SnO\cdot H_2O$ Air-dried		E $2SnO\cdot H_2O$ Dried 110°C		F α-SnO from $2SnO\cdot H_2O$	
D	I	D	I	D	I	D	I	D	I
4.79	4	3.38	10	3.53	10	3.52	10	4.79	4
2.96	10	2.99	5	3.32	10	3.32	10	3.37	2
2.68	5	2.92	5	2.99	10	2.98	9	2.97	10
2.40	3	2.88	9	2.82	9	2.79	9	2.68	5
1.890	4	2.66	9	2.64	1	2.51	4	2.40	3
1.787	7	2.08	1	2.51	4	2.40	4	1.90	4
1.595	9	2.02	4	2.40	4	2.27	3	1.795	7
1.482	8	1.769	8	2.27	3	1.925	5	1.595	9
1.369	1	1.675	2	1.925	5	1.771	5	1.489	8
1.336	2	1.595	2	1.776	5	1.691	1	1.339	2
1.220	1	1.496	2	1.690	1	1.624	1	1.221	1
1.195	1	1.414	2	1.625	1	1.575	1	1.168	3
1.165	3	1.294	2	1.572	1	1.466	1	1.100	1
1.099	1	1.204	2	1.406	1	1.405	1	1.074	2
1.072	2	1.096	2					1.026	2
1.027	2							0.993	1
1.018	1							0.899	1
0.992	1							0.882	1
0.932	1							0.847	1
0.900	1							0.838	1
0.879	1							0.802	1
0.872	1							0.750	1
0.850	1								
0.839	1								
0.798	1								
0.749	1								
0.712	1								

forms: α-SnO, the blue-black tetragonal form which is brownish-green when in a finely-divided state; and β-SnO, the greyish-green modification prepared by heating the α-SnO to above 550°C.

Hydrous Hydrated Stannous Oxide.

Stannous oxide hydrate was precipitated from a freshly prepared and filtered HCl solution of $SnCl_2$ by the addition of NH_4OH. Upon the addition of the NH_4OH the temperature rose from that of the room to about 60°C. The white or faintly yellow colored, hydrous precipitate was washed first with ammonia and then with water by centrifuging at 3000 r.p.m. until peptization began. A very stable sol resulted before the precipitate was chloride free; centrifuging for over an hour at 3000 r.p.m. failed to produce coagulation. Accordingly, further purification was carried out by washing with a supercentrifuge at 36000 r.p.m. After repeated washing only a trace of chloride remained. The precipitate was then air-dried until it could be powdered, and a sample was placed in a weighing bottle and was dehydrated by heating in an electric oven in a stream of dry nitrogen, which was purified by passing through a heated pyrex combustion tube containing copper freshly reduced by hydrogen from cupric oxide wire. The nitrogen was not rendered completely oxygen free, since continued heating at high temperatures resulted in some oxidation of the oxide. However oxidation is negligible in the temperature range for which results are reported. The isobaric temperature-composition curve that was obtained with three separate samples is plotted in Fig. 2. The composition when dried in the manner described at 50°C was found to be, % SnO: observed 93.70, 93.71, 93.74; calculated for $2SnO \cdot H_2O$, 93.74. It is apparent from the form of the curve that the hydrated SnO has the composition corresponding to the hemihydrate, $2SnO \cdot H_2O$. As the dehydration proceeds, the sample becomes decidedly yellow by the time the temperature reaches 100°; at higher temperatures a grey or green color appears. The change in color from the white or faintly yellow to the permanent deeper yellow, is a continuous one. The nature of this change will be discussed in the second paragraph following.

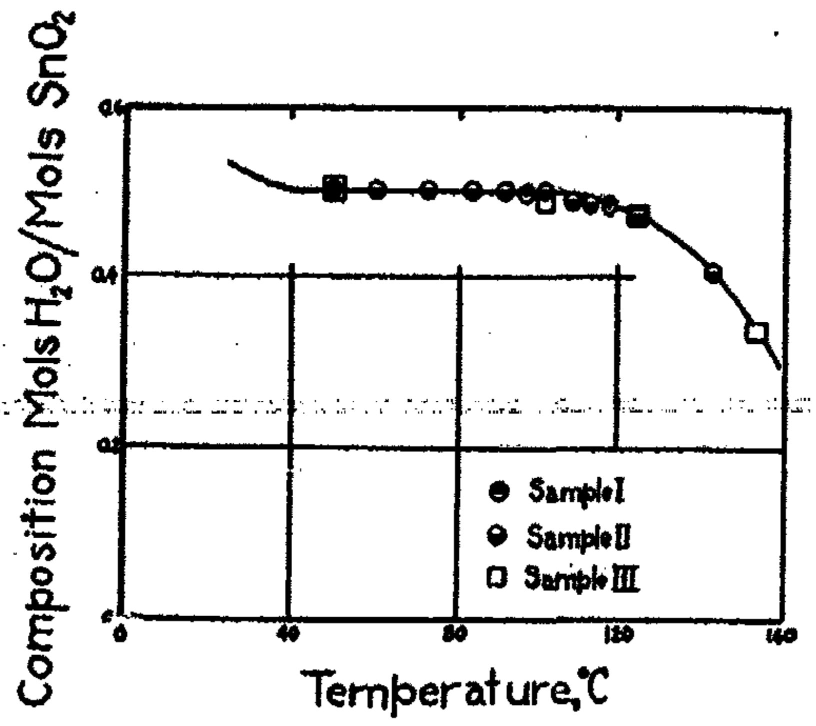

FIG. 2

Composition-Temperature Curve of Stannous Oxide Hemihydrate

X-radiograms were obtained for the following samples: *D*, $2SnO \cdot H_2O$, air-dried; *E*, $2SnO \cdot H_2O$, dried at 110°; and *F*, α-SnO prepared by heating $2SnO \cdot 2H_2O$ to about 400° in a vacuum. The results are given in Table II and Fig. 1. For purposes of comparison, *G*, the pattern of SnO_2 is also included in Fig. 1. It will be observed that the crystal structure of the hemi-hydrate is different from either the α-SnO or the β-SnO, and that the product of thermal decomposition is α-SnO, provided the temperature is kept below 550°C, the transition temperature for the α to β transformation.

Since the x-radiograms for hemi-hydrate dried in the air and at 110° are the same, the change in color from white or faintly yellow to decidedly yellow, cannot be due to isomerism; but must be due to a change in particle size or physical character. From the width of the lines on the x-radiograms, it appears that the deep yellow material has the larger particles. Thus crystal growth takes place as the hemi-hydrate is heated.

Blackening of Hydrated SnO on Exposure to Light. Stannous chloride in slight excess was treated with NH_4OH in a pyrex flask in the dark. Test tubes were filled with portions of the suspension and stoppered and aged as given in Table III. The samples exposed to light were left in a test-tube rack in ordinary daylight. The others were kept in a closed cupboard in a dark room, and were examined at intervals. Inspection of Table III makes it clear that the nature of the containing vessel has little or nothing to do with the darkening; but that it is caused by the action of light. In order to test further the effect of light and the effect of the nature of the surface of the containing vessel, another experiment was carried out. Hydrated SnO was precipitated from a slight excess of $SnCl_2$ by NH_4OH in a pyrex flask in diffused daylight. Within 5 minutes after precipitation, samples were placed in soft glass cylinders treated as in Table IV.

TABLE III

Container	Color after							
	Kept in dark				Exposed to light			
	5 min.	2 hrs.	1 wk.	2 wks.	5 min.	2 hrs.	1 wk.	2 wks.
Soft glass	white	white	white	white	white	grey	green-grey	green
Pyrex	white	white	white	white	white	grey	green-grey	green
Fused silica	white	white	white	white	white	grey	green-grey	green

TABLE IV

Time	Color after							
	Exposed to light				Kept in dark			
	New cylinder washed with		Scratched cylinder washed with		New cylinder washed with		Scratched cylinder washed with	
	HCl	NaOH	HCl	NaOH	HCl	NaOH	HCl	NaOH
5 min.	white	white	white	white	white	white	white	white
15 min.	grey	grey	grey	grey	white	white	white	white
1 da.	green	green	green	green	white	white	white	white
3 da.	green	green	green	green	white	white	white	white
1 wk.	green	green	green	green	white	white	white	white

The coloration begins on the side of the glass nearest the most intense illumination. In each of the above described series of experiments, a portion of each precipitate was made alkaline with NH_4OH and allowed to stand in the light in a pyrex flask. Only slight darkening takes place, and the original white or faint yellow may become slightly deeper. As is well known, a solution of $SnCl_2$ in dilute HCl hydrolyzes, precipitating out a white, creamy substance upon standing. Since in the experiments described, an excess of $SnCl_2$ is present, one would expect the same thing to happen; and such is the case. However, there is no danger of confusion as to color, as the deposit forms in a separate thin, upper layer.

Two samples (not included in the tables) one with a slight excess of $SnCl_2$ and the other with a slight excess of NH_4OH, after standing several weeks, contained some blue-black crystals which were proven by microscopic and x-ray examination to be α-SnO. It is apparent that the blackening process consists of a transformation of the white or faintly yellow $2SnO \cdot H_2O$ first to anhydrous α-SnO in the finely-divided greenish-brown form, and second to blue-black α-SnO as the particles increase in size. This dehydration is accelerated by the action of light, especially in the absence of free ammonia. The nature of the containing vessel and its surface is of minor if not of negligible importance. The failure of Bury and Partington to observe darkening in silica was probably due to their use of an opaque vessel.

Summary

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

1. Stannous oxide has been found to exist in two polymorphic forms: α-SnO which is blue-black in large crystals and brownish-green when powdered; and β-SnO which is greyish-green. The transition temperature from the α to the β form is approximately 550°C.

2. The crystal structure of α-SnO is tetragonal, of the PbO type with $a_0 = 3.78$ Å and $c_0 = 4.79$ Å.

3. The precipitate formed by the interaction of solutions of a stannous salt and NH_4OH has been found by a temperature-composition isobar and x-ray diffraction studies to be the hemihydrate, $2SnO \cdot H_2O$.

4. Stannous oxide hemihydrate is dehydrated into α-SnO by (a) the action of excess alkali, (b) the action of light especially in the absence of free ammonia, and (c) heating to temperatures above 120° and below 550°.

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THE SORPTION OF VAPORS ON WOOD AND CELLULOSE

BY N. H. GRACE* AND O. MAASS

The following study of vapor sorptions by cellulose and cellulose materials** makes use of a quartz spring balance suspended in an evacuated glass system. Advantages are claimed for the special technique employed. The results of water vapor sorption on various species of woods are given and compared with the sorption on cotton cellulose. The main feature of this paper, however, deals with the sorption of hydrogen chloride on cellulosic materials in the presence of previously absorbed water, because of the information this gives regarding the mechanism of sorption on such materials. The sorption of a number of other vapors is tabulated.

The sorption of water vapor on cotton has been studied extensively in the Shirley Institute and in the Eastman Kodak Laboratories under the direction of Dr. Sheppard, their results are recognised by the authors as fundamental. Hence, allusions to determinations made with cotton may be taken as being for purposes of comparison. However, certain advantages are claimed for the experimental method described by the authors, which is unique (in this sense) that where adsorption or desorption values are determined, these are carried out at a constant vapor pressure in the case of water vapor. Furthermore, the small amount of sample which can be examined gives results which are believed to be more nearly absolute, and therefore more comparable with determinations of Sheppard and Newsome[1] who use the quartz spring balance although they do not use the same experimental procedure of maintaining constant vapor pressure. A comparison, however, of the results obtained by various experimenters and an explanation of differences obtained, is to be left to another paper which will be published shortly.

As in the case of the investigations carried out by Pidgeon and Maass,[2] this paper must be considered as striving to deal with data in a new field, that of the sorption of vapors on wood and of using sorption values on other cellulosic materials for purposes of comparison, in order to obtain information on the properties of cellulose as it exists in wood.

The term sorption is used to indicate the amount of sorbed substance on the basis of percentage composition of the system. The term absorption is used to indicate the amount of sorbed substance on the basis of percentage composition of the system when the system previous to the determination contained a considerably smaller amount of sorbed vapor. The term desorp-

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* The work described was carried out under the tenure of two scholarships granted by the National Research Council of Canada.

** This research was carried out in the Institute of the Pulp & Paper Association as a part of "Penetration Studies" under the direction of Dr. Maass. It was also included in the research programme of the Forest Products Laboratory at Montreal.

[1] J. Phys. Chem., 33, 1817 (1929).

[2] J. Am. Chem. Soc., 52, 1053 (1930).

tion is used to indicate the amount of sorbed substance on the basis of percentage composition when the system previous to the determination contained a considerably larger amount of sorbed vapor. In the desorption values given for water vapor on wood the reader is referred to the article quoted in which the determinations are described in detail.

Experimental

Fig. 1 indicates the essential features of the system in which sorption occurs. Actually, several different units have been employed in this investigation. These were modified to meet the particular requirements of special cases; there has, however, been no important variation in principle.

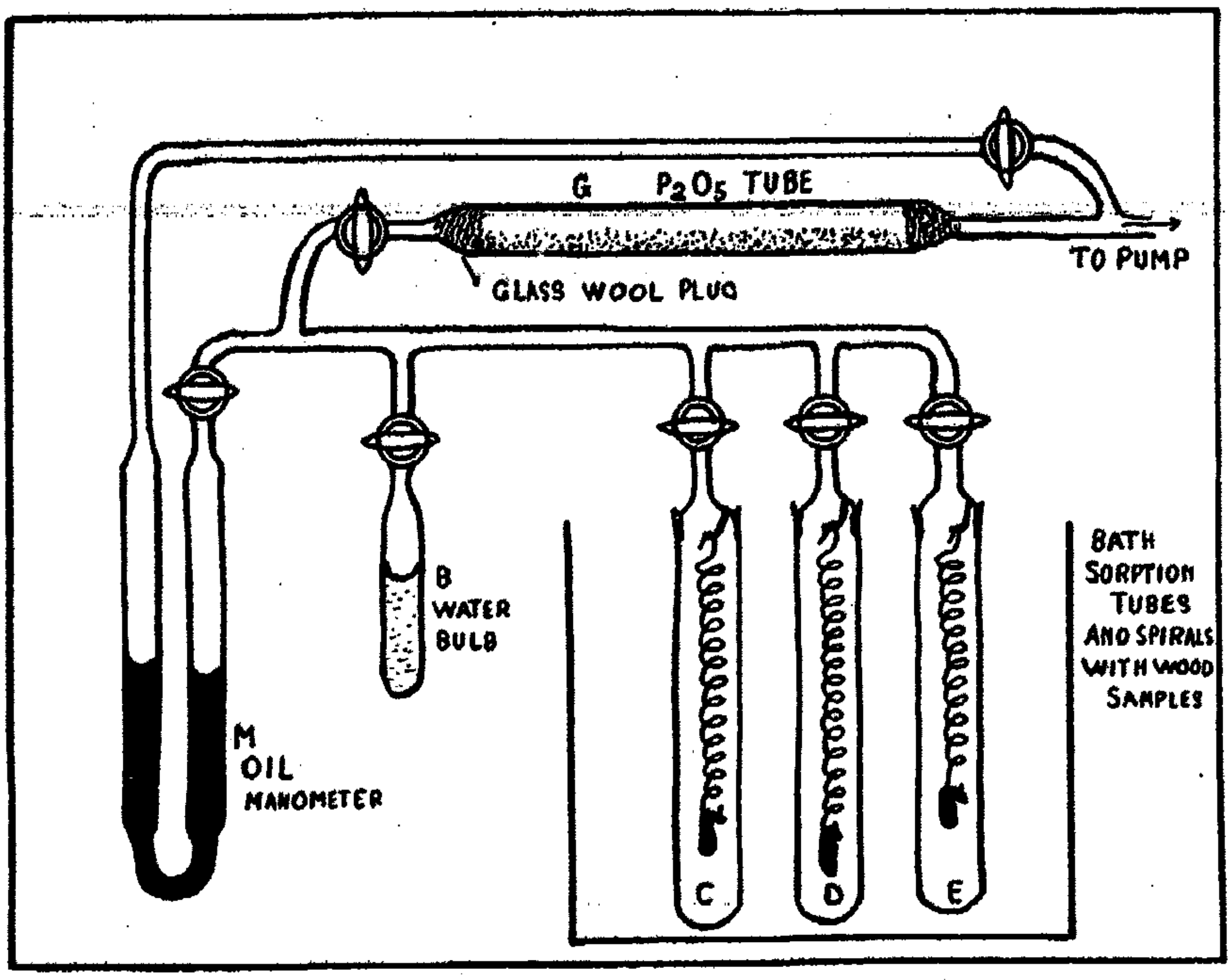

Fig 1

The glass tubes *C*, *D*, and *E*, are removable, the ground glass joints are indicated in the diagram. The tubes are about eleven inches in length, with an inside diameter of one inch. A small glass hook, sealed into the glass head, serves as a support for the quartz spring balance. These tubes have functioned in a satisfactory manner as containers for spiral and sample. No tendency to leak at the large ground-glass joint has been observed. In the case of the tubes most recently placed in service any possibility of leakage has been eliminated by the presence of a flange on the tube, this may be filled with mercury. Another improvement, not indicated in the diagram, is a change in the position of the connecting tube. By inserting this in the side of the large tube the ground-glass top may be removed without removal of the thermostating bath. The diagram indicates three sorption chambers in series. In practice it has been found convenient to use as many as 6 of these together. This system was confined to a study of the water vapor equilibria of woods and cottons.

The tube *B* contains water and serves as a source for vapor. It is surrounded by a Dewar flask maintained at a constant temperature, and thus the vapor pressure may be controlled.

The oil manometer is shown *M*. The oil used is "Cenco Hyvac" pump oil, and has a density about 1/15 that of mercury, and also a negligible vapor pressure. This enables ready and accurate observation of the vapor pressures of water in the system. Where gases are used which require the measurement of greater pressures than can be indicated by this oil manometer, or with which chemical action may occur, substitution is made for the oil manometer *M*, of a mercury manometer. This is capable of indicating pressures up to 80 cms. of mercury.

The position of a phosphorus pentoxide tube *G* is indicated in the diagram, it is used in the determination of the dry weight of the sample. Further, the tube takes up water very readily, thus avoiding the actuation of the pumping system for the removal of small amounts of water vapor.

The bath surrounding the sorption tubes is indicated by the heavy lines. The bath in use consists of a container with a flat plate glass surface. An aquarium, of suitable size to accommodate a battery of 6 sorption tubes, has been found quite satisfactory. The bath is equipped with a stirrer which ensures rapid and thorough circulation. The heating element is controlled by a toluene mercury thermo-regulator through a relay. This regulates the temperature in a satisfactory manner, the maximum fluctuations being in the neighborhood of 0.02°C. Further, a cooling coil of lead piping through which a variable stream of cold water circulates, permits the use of temperatures which are below those of the room, thus increasing the temperature range over which investigation may be conducted.

The pumping system consists of a Langmuir mercury condensation pump backed by a Hyvac. The gas pressure in the system is determined by means of a MacLeod gauge which is capable of indicating pressures down to 0.0005 mm of mercury. In all experiments the pressure is first lowered to at least 0.001 mm before a run is commenced.

Observation of the extensions of the quartz spring balance is made by a cathetometer. The instrument used is capable of giving readings accurate to 0.02 mm. Spirals were constructed from quartz after the method of McBain and Bakr.[3] The spiral is calibrated throughout the working range by observing the deflections caused by known weights. On the average a deflection of 1 mm corresponds to a weight of 0.0030 g. Thus, with the particular cathetometer employed, a weight of 0.0001 g can be easily detected, and the total weight of a sample weighing 0.1 g can be determined accurately to within 0.1%.

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[3] J. Am. Chem. Soc., 48, 690 (1926).

Since the maximum differences observed are not greater than 30% of the total weight, the theoretical accuracy is well within 0.5% of the differences noted.

The sample is dried by long evacuation in the presence of phosphorus pentoxide at a pressure of about 0.0005 mm mercury. After approxmately 12 hours a constant weight is observed. This weight is arbitrarily considered as the "dry weight," and the percentage increase due to sorption is always calculated on this basis. This point is completely reproducible, and may be checked several times, even after the sorption of water vapor. However, this reproducibility is not always found when other gases are used. It only holds when the sorbing system suffers no permanent change.

The Sorption of Water Vapor

The details of experiment and the results of water vapor sorption by cellulose and woods will be found in the Canadian Journal of Research. The following will merely touch on the most important conclusions of this work.

An attempt was made to correlate the "variation in the sorption" of the various woods with some of their other physical properties, such as density and hardness, but without success. The most important generalization to be found, is the great similarity in the amount of sorption for all the woods, twenty in number, examined to date. The desorption isotherm was found to be the least variable property of the woods examined, its variation from wood to wood being small.

It is of interest to note that of the 20 woods examined, in 11 the heartwood has the greater sorption, in 6 they are approximately the same, and in only 3 is there distinctly greater sorption in the sapwood. This means that, as a rule the heartwood has a greater sorption than the sapwood. Below is given a table which contains average sorption values. From this it will be seen that

TABLE I

Average Desorption Values for Woods and Cottons—% Sorption

Relative Humidity %	17.3	51.8	86.4
Vapor Press. mm, Hg.	3	9	15
Average Values for Twenty Species of Wood			
Sapwood	4.90	10.50	19
Heartwood	5.20	11.10	20.4
Average	5.05	10.80	19.70
Values for Extracted White Spruce			
Sapwood	5.25	10.70	21.25
Heartwood	5.00	10.10	19.10
Average	5.10	10.40	20.20
Values for Cotton Cellulose			
Cotton (1).	2.80	5.70	12.15
Cotton (2).	3.30	6.85	13.30

the heartwood has a somewhat greater sorption than the sapwood on the average.

The values obtained for extracted wood are for two samples which gave practically identical values. The extraction was carried out in a standard manner, refluxing for several days in 1% sodium hydroxide in an atmosphere of nitrogen.

The desorption values for cotton (1) were determined on a rag cotton obtained from Eastman Kodak Co., and which had been subjected to careful purification. The values for cotton (2) are the desorption values obtained by Urquhart and Williams.[4]

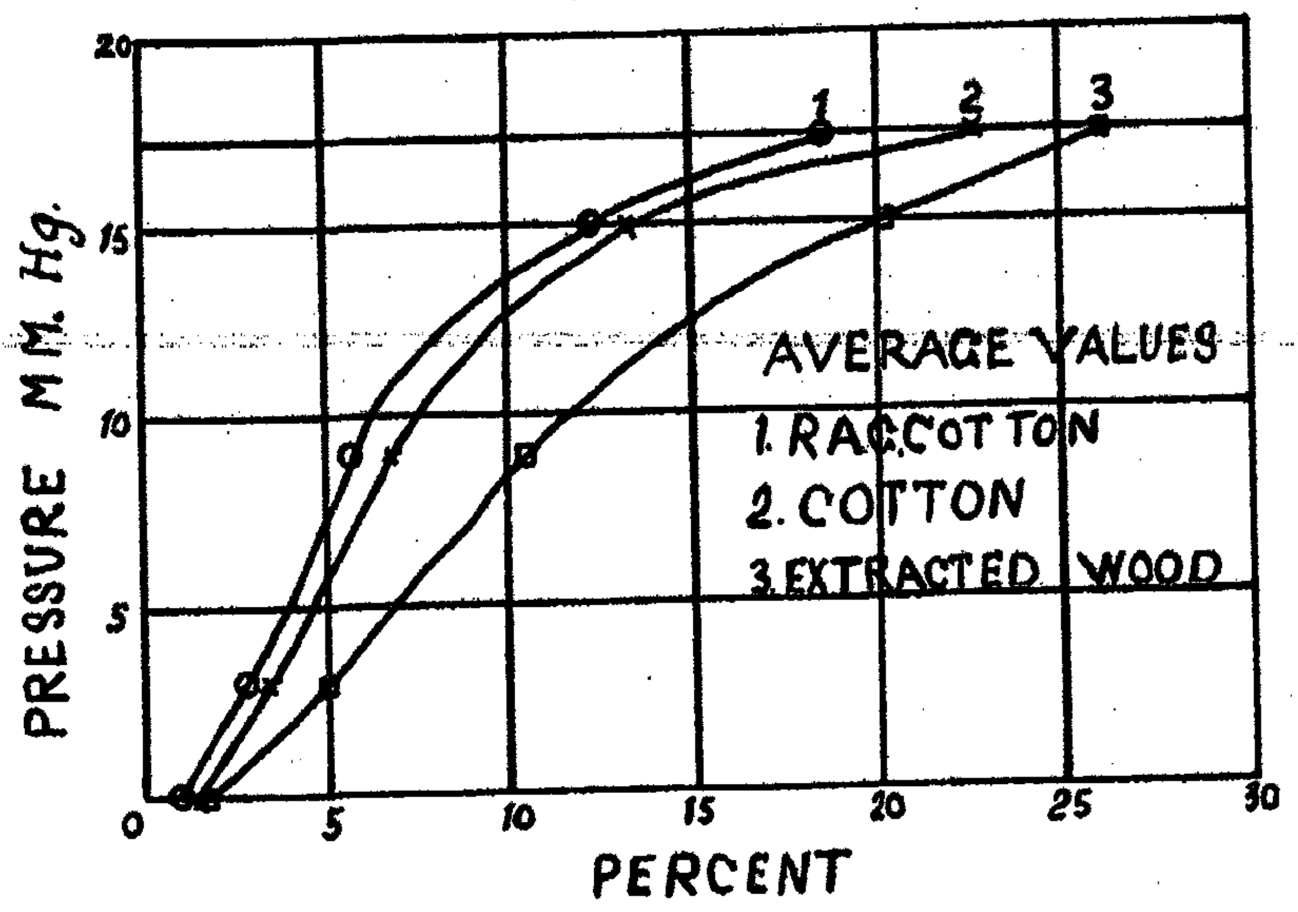

Fig. 2
Sorption of Water Vapor

Figs. 2 and 3 give a graphical representation including the data listed above. It is clearly shown that the extraction, which has removed all the carbohydrates, resins etc. and left only the cellulose and most of the lignin, has reduced the sorption by only very little. This reduction is, for the most part, in the region of high relative humidity, where the gross structure of the material plays a part.

It follows definitely, that the experiments of Pidgeon and Maass[2] have been corroborated as far as these showed that the sorption of water vapor by wood is on a much greater scale than the sorption by cotton. This is true over the whole range of vapor pressures, both for the wood in its natural state, and for the extracted samples.

The discussion of sorption values at 100% relative humidity and at 0% humidity is left to another paper, although these are shown in the graphs. Sufficient to say here that these are extrapolated values and not to be compared with experimentally determined ones.

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[4] Shirley Institute Memoirs, 3, 197 (1924).

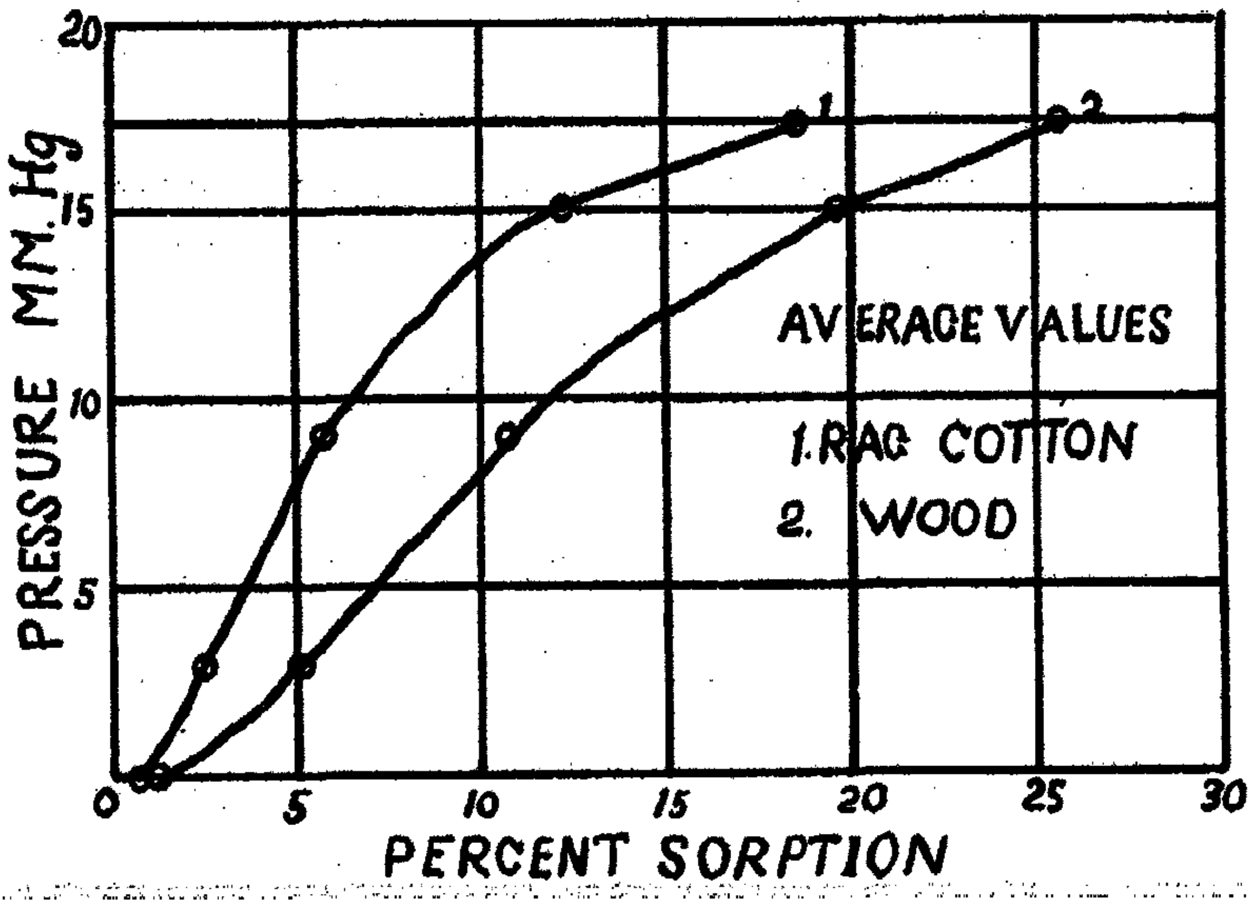

Fig 3
Sorption of Water Vapor

The Sorption of Hydrogen Chloride by Wood and Cellulose

When cellulose is brought into an aqueous solution of hydrogen chloride it hydrolizes, the cotton undergoes a marked change in physical properties. No measurements of the sorption of hydrogen chloride gas in cotton and wood, as far as the authors know, have been carried out. In view of the change mentioned above, such an investigation is of interest.

It should, perhaps, be mentioned that most carefully prepared anhydrous hydrogen chloride was used. The gas was bubbled through 2 wash bottles of concentrated sulphuric acid, and finally over 2 phosphorus pentoxide tubes. This ensured a perfectly dry sample of gas coming into contact with the wood and cotton under investigation.

The first experiments attempted were with a dry cotton, and it soon became apparent that equilibrium was only brought about after a very long time. Below are the sorption values that were obtained. From the flattening out of the time curve they are supposedly equilibrium values, each is the result of a 90 hours experiment. It is seen that quite appreciable amounts of HCl are absorbed.

Sorption of Hydrogen Chloride by Cotton Cellulose.

Equilibrium value at 5.40 cm press. of gas 0.80%.

Equilibrium value at 70.20 cm press. of gas 2.00%.

Sorption against Time

Time (hours)	% Sorption	Time (hours)	% Sorption
17	1.26	70	1.90
28	1.49	87	1.95
52	1.61	94	1.95
64	1.83		

(Final gas pressure 70.20 cm. Temperature 22°C)

On applying the vacuum, the HCl came off fairly readily until 0.80% was left. There had been little change in the appearance of the sample. Only at the higher HCl pressure did it take on a greyish tinge. On heating in vacuo, at 50°C the last trace of HCl was driven off, and the original weight of the sample was reached. It was judged that the HCl was absorbed by the cotton and could be desorbed, but the time required for equilibrium to be reached, made it impractical to carry out a detailed sorption isotherm.

When the cotton was replaced by a sample of white spruce heartwood, it was found that equilibrium was established much more rapidly, only one third of the time being required. The equilibrium values for sorption are given below, and also the data for a typical time curve. Column 1 indicates that 2 samples were used, and the sorptions obtained (col. 2) at various pressures of HCl (col. 3) are shown in Fig. 4 to lie on a smooth curve. To test out desorption sample 1, after having been maintained at a pressure of 76.90 cm was kept until equilibrium resulted at a pressure of 35.40 cm. This gave a desorption value of 8.97%, which it is seen, lies fairly well on the absorption isotherm, indicating that there is little or no hysteresis. This, of course, will have to be confirmed when time permits. In a vacuum the absorbed HCl was taken out fairly rapidly until a residue of 2.24% was reached after 24 hours.

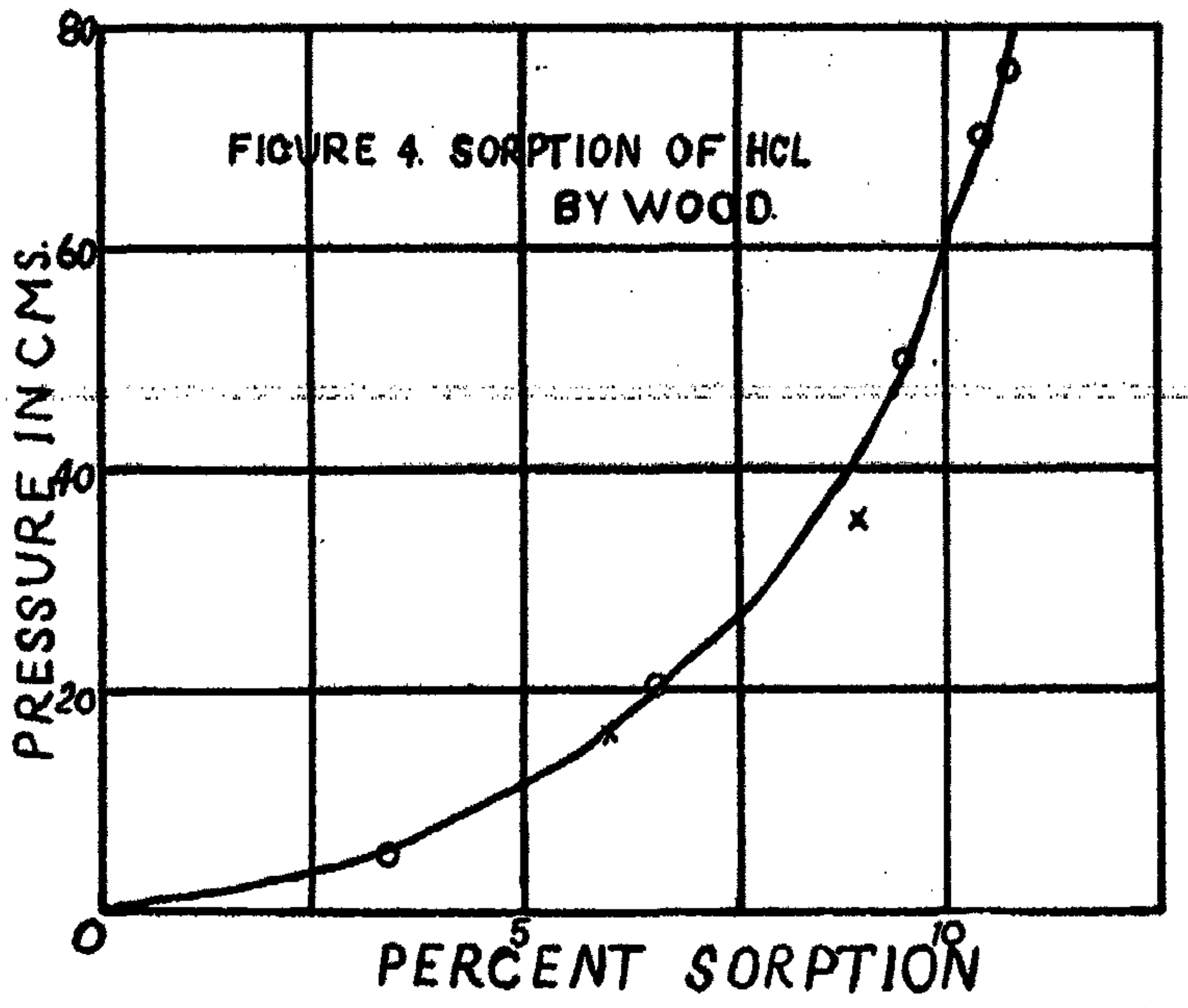
FIGURE 4. SORPTION OF HCL BY WOOD.

The form of the isothermal sorption curve is apparently quite different from the sorption curve with water vapor, and approaches more nearly to the form of a Freundlich adsorption. It is true that in terms of relative vapor pressure—as far as HCl is concerned—it is only a small fraction of the saturation value that has been examined. But the criterion for similarity is found in the sharp upturn of the curve. Before discussing this phase any further it is

Sorption of Hydrogen Chloride by White Spruce.

Sample	% Sorption	Pressure (cm Hg)	Sample	% Sorption	Pressure (cm Hg)
1	3.38	5.50	2	10.71	76.90
1	7.60	20.09	Desorption Equilibrium Values		
2	9.40	49.60	1	8.97	35.40
1	10.37	70.60	2	7.01	16.00

(Temperature 22°C)

Sorption against Time

Time (Hours)	% Sorption	Time (Hours)	% Sorption
½	2.54	10	6.02
2	4.08	21	6.72
3	4.43	24	6.93
4	5.23	27	7.32
5⅛	5.53	31	7.42
7⅔	5.83		

(Final pressure 20.09 cm. Temperature 22°C)

Desorption of Hydrogen Chloride against Time.

(Initial value 10.71% HCl)

Time (Hours)	% Sorption	Time (Hours)	% Sorption
¼	8.57	3¼	4.83
½	7.67	7	3.13
1	6.82	13	2.74
1¾	5.63	23½	2.24

worth considering the experiments carried out with wood samples containing a definite amount of water, because in these cases, also, sorption curves were obtained similar in character to that of hydrogen chloride in dry wood.

The experimental procedure consisted in suspending a sample from the spiral and first of all bringing it down to dry weight. Then water vapor was brought into contact, until a desired amount of sorption had taken place. The stopcock, leading to the water bulb, was then closed, and HCl admitted to the desired vapor pressure. The latter was always many times that of the residual water vapor remaining in the apparatus, so that further absorption of water vapor could be neglected in comparison to the striking increase in sorption, which is to be discussed. A calculation shows that the maximum possible error due to all residual water being absorbed is in the order of 1/2% of the dry weight of wood, and it is very unlikely that this would be reached. The direction in which error would take place would be, of course, to give an added apparent sorption of HCl. As a matter of fact, the addition of HCl will sweep any residual water vapor on to the walls of the containing vessel. This was made apparent in the case of highest water vapor pressure by the formation of a very fine mist. The experimental results follow.

TABLE II

Sorption of HCl by White Spruce containing absorbed water

% HCl	% HCl (held by H_2O)	% HCl (in wood)	V.P. (cm Hg)
(Amount of water absorbed by the wood .... 1.67%)			
5.38	0.86	4.52	11.60
8.83	1.04	7.79	40.60
11.22	1.16	10.06	74.70
(Amount of water absorbed by the wood .... 3.29%)			
5.24	1.64	3.60	5.30
6.97	1.73	5.24	11.00
8.40	1.82	6.58	21.30
10.26	2.19	8.07	40.70
11.24	2.37	8.87	76.00
(Amount of water absorbed by the wood ... 5.05%)			
10.50	2.49	8.01	11.70
13.08	3.04	10.04	41.00
14.22	3.36	10.86	73.00
(Amount of water absorbed by the wood ... 7.46%)			
11.55	3.82	7.73	9.70
15.63	4.70	10.93	41.00
17.17	5.22	11.95	74.30
(Amount of water absorbed by the wood ... 9.47%)			
15.74	5.16	10.58	11.50
19.74	6.13	13.61	43.70
22.46	6.84	15.62	73.80
(Amount of water absorbed by the wood .. 12.30%)			
18.45	6.27	12.18	9.50
24.28	7.74	16.54	41.20
27.04	8.61	18.43	72.40

The first column in the above table indicates the amount of HCl taken up by the system wood-water. The second column indicates the amount of HCl calculated as dissolved in the water present, on the assumption that the water is unaltered. (The calculation is made from data found in Landolt-Börnstein, page 1397). The third column represents the actual sorption by the wood. It is obtained by subtracting the amount of HCl, calculated as existing in solution in the absorbed water, from the total amount of sorbed HCl. The fourth column indicates the HCl pressure at which the equilibrium point was determined.

It is of interest to note that the equilibrium sorption values were reached more rapidly with wet wood than is the case with dry wood. The difference is most striking with wet and dry cotton. Whereas 90 hours were required with the dry cotton (the data have already been given), 3 hours sufficed when water was present. The data for a typical case follow.

The Sorption of HCl by Cotton with Absorbed Water.

Sorption against Time

(Amount of water absorbed by the cotton . . . . 2.92%)

Time (hours)	% HCl Sorbed	Time (hours)	% HCl Sorbed
¼	2.91	1½	4.15
½	3.39	2	4.24
1	3.86	3	4.33

(Final gas pressure was 10.40 cm Hg)

On raising the pressure of HCl to 41.50 cm Hg the following gives the sorption.

Time (hours)	% HCl Sorbed	Time (hours)	% HCl Sorbed
1	5.46	6	5.93
2	5.65	8	5.90

In the case of the wet wood samples evacuation brought the weight down to within 2% of the dry weight. After heating to 50°C a semi-permanent increase of 1% was still observed. In the case of cotton, heating reduced the residual increase of 4.6% to an actual loss of 1.3% showing that some permanent change has taken place. However, a water sorption isotherm on such a sample showed very little change, except at the initial stage, where there was a decreased absorption. If the comparison is made with the initial sorption, of a specially purified cotton, this is not so great. (The comparative data follow.) In the case of wood, only the first part of the water sorption isotherm was examined, and this, as with the cotton, showed a small decrease in the water absorption of the hydrogen chloride treated wood.

The Sorption of HCl by Cotton containing Absorbed Water.

% HCl	% HCl (In water)	% HCl (By cellulose)	V.P. (cm Hg)
(Amount of water absorbed by the cotton . . . . 2.92%)			
4.42	1.45	2.97	10.40
5.93	1.86	4.07	41.50
6.49	2.04	4.45	74.50
(Amount of water absorbed by the cotton . . . . 4.32%)			
6.90	2.20	4.70	9.90
9.20	2.72	6.48	41.60
9.93	3.02	6.91	75.20

The Water Sorption of HCl-treated Moist Cotton as contrasted to that which is untreated.

% Sorption		Relative	% Sorption		Relative
Untreated	Treated	V.P. (%)	Untreated	Treated	V.P. (%)
1.00	0.60	10	5.55	5.40	60
1.60	1.20	20	6.35	6.60	70
2.40	2.25	30	7.40	8.00	80
3.40	3.30	40	8.45	10.00	90
4.35	4.30	50	11.00	12.80	100 (extrap)

By means of the data contained in the preceding pages, a composite table can be formed, giving interesting information. This is given below.

TABLE III

The Sorption of HCl by White Spruce Heartwood

% Sorption							V.P.
0%	1.67%	3.29%	5.05%	7.46%	9.47%	12.30%	(cm Hg)
3.20	3.20	3.35	6.40	7.00	9.30	11.15	5
5.70	4.25	4.90	7.67	7.85	10.20	12.20	10
7.40	5.60	6.52	8.87	9.15	11.50	13.95	20
8.27	6.80	7.50	9.45	10.00	12.55	15.30	30
8.90	7.72	8.05	9.98	10.70	13.35	16.35	40
9.35	8.55	8.37	10.37	11.20	14.05	17.20	50
9.86	9.25	8.60	10.62	11.55	14.75	17.90	60
10.36	9.90	8.79	10.80	11.70	15.40	18.35	70
10.54	10.10	8.87	10.87	11.90	15.80	18.50	75

This table is made up of values read off curves plotted for each of the runs which have just been given. Each column is headed by the percentage of water present. Since the first column gives values for the sorption of HCl by dry wood, and since all the other values have been corrected for the acid held by the water, reading across in a horizontal manner one observes a range of HCl sorptions at one gas pressure, but by samples with different amounts of absorbed water.

These results can be interpreted in a number of ways, and it is rather difficult to decide which is the correct interpretation. Suppose, first of all, one considers the water absorbed by the wood to be unchanged in its power to dissolve HCl. Then the values in the table, which were calculated on this basis, show that in samples having less than 4% of absorbed water, the wood sorbs less HCl, while above 4% it sorbs more HCl, than the dry sample. On the other hand one might assume that the sorption of HCl, on wood is unaltered, and that the absorbed water has changed in relation to its capability of dissolving HCl. This would mean that the water absorbed in samples containing the highest percentages of water, dissolved HCl better than ordinary water. The water absorbed to high percentages is, however, more likely to retain its usual characteristics than the first water that is absorbed. Doubtless the first 1 or 2% of water absorbed by wood will not have the same solvent action on the HCl as ordinary water, but with increased water content the ordinary water properties should be approached more and more by the absorbed water.

Recent work by Filby and Maass* on the density of water sorbed by cellulose is of interest in this connection. The variation in hydrogen chloride sorption for wood containing about 4% sorbed water has its counterpart in the density change observed in this same region for water sorption by cotton cellulose. It has been shown that the first few % of water sorbed by cellulose has a density of 2.4. This high density is constant at first and then falls with further sorption until it becomes asymptotic to the value 1. This would indicate a very intimate relationship existing between the first few % of sorbed water and the sorbing material.

It is not surprising, in the light of this density change, that the first few % of sorbed water form a system which absorbs less hydrogen chloride than the two components alone. The subsequent addition of water beyond 4% results in greatly increased surface due to swelling action. This will be amplified below.

Some experiments carried out on HCl sorption by samples containing water left after desorption had taken place, are interesting in connection with what was said above. Two samples were first of all saturated with water vapor, then desorption was allowed to take place until a value was reached, as near as possible to an absorption value. The experimental data are given below. Following this a table is given in which 5.40% desorption is compared with a 5.05% absorption, and a 7.88% water desorption value is compared with an absorption one of 7.46%.

The Sorption of HCl by Wood containing Desorbed Water Vapor.

% HCl	% HCl (Held by water)	% HCl (By wood)	V.P. (cm Hg)
	(Amount of desorbed water .... 7.88%)		
9.85	4.01	5.84	9.30
14.17	4.99	9.18	42.60
16.08	5.50	10.58	74.13
	(Amount of desorbed water ...... 5.40%)		
8.16	2.74	5.42	9.40
12.33	3.34	9.01	39.10
14.21	3.76	10.45	71.00

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* Can. J. Research, 7, 162 (1932).

TABLE IV

Sorption of HCl by White Spruce Heartwood following Adsorption and Desorption of Water Vapor

% Sorption				
5.05% (Abs)	5.40% (Des)	7.46% (Abs)	7.88% (Des)	V.P. (Cm Hg)
6.40	4.30	7.00	5.35	5
7.67	5.35	7.85	6.00	10
8.87	7.00	9.15	7.15	20
9.45	8.15	10.00	8.20	30
9.98	9.00	10.70	8.95	40
10.37	9.60	11.20	9.60	50
10.62	10.10	11.55	10.10	60
10.80	10.45	11.70	10.50	70
10.87	10.60	11.90	10.60	75

Each column is headed by the percentage of sorbed water.

From the results of Table III the amount of HCl sorbed increases with the amount of water present, above the 4% sample. Thus, if the fact of the equilibrium water value being absorption or desorption is of no consequence, one would naturally expect the two "desorption" woods to take up the largest amount of HCl, as each exceeds the "absorption" value by about 0.40%. However, both woods with the larger amount of water—but present as equilibrium desorption values—sorb decidedly less HCl than the woods with less water—but water present through absorption. Apparently the wood has a lessened ability to take up acid when the water exists there following absorption.

In the above table (Table IV) is given the percentage sorbed on the dry wood, that is, after the HCl dissolved in the water has been subtracted, as was described before. Before discussing the reason for this, it is necessary to see whether any information can be obtained with regard to the nature of the HCl sorption.

As was pointed out before, the absorption curve for HCl has a different form from that of the water sorption isotherm. If both of these are tested by applying Langmuir's adsorption formula

$$x/m = abp/(1+ap).$$

it is found that the water sorption does not follow this, whereas the HCl sorption of both dry and wet wood does, it also holds for HCl sorption by wet cellulose. In Fig. 5 curve 1 represents the sorption of water in cellulose, and 2 that of HCl by wet cotton cellulose. According to McBain[6] the interpretation that is given is that in the case of HCl we are dealing with a straight surface adsorption, whereas in the case of water, part, at least, must be due to filling up of the interstices between the actual cellulose and part to adsorption. If the HCl sorption is surface adsorption, then the interpretation that can be

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[6] J. Am. Chem. Soc., 52, 2668 (1930).

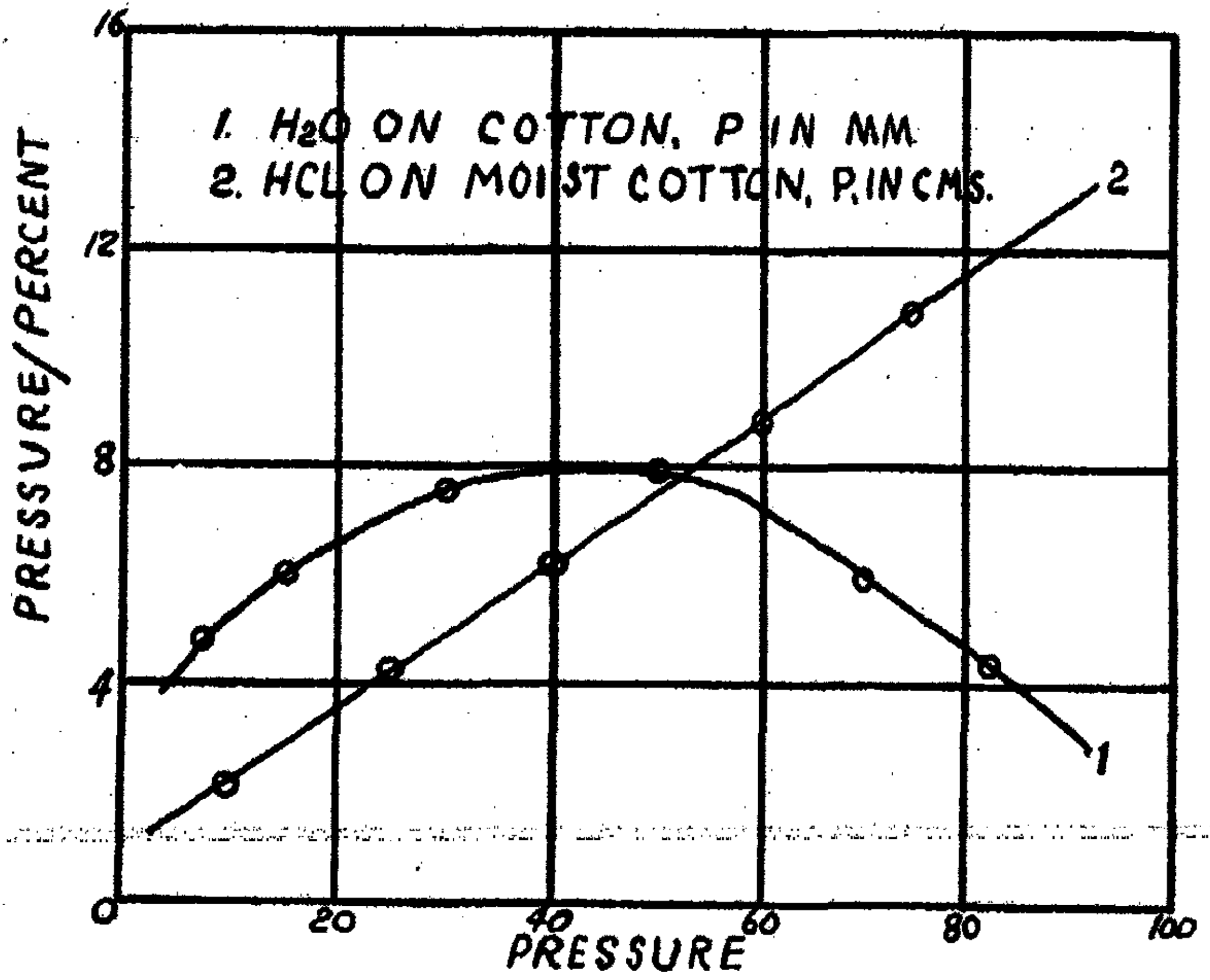
1. H_2O ON COTTON, P IN MM
2. HCL ON MOIST COTTON, P, IN CMS.
PRESSURE/PERCENT
PRESSURE
0
4
8
12
16
20
40
60
80
100
1
2

Fig. 5

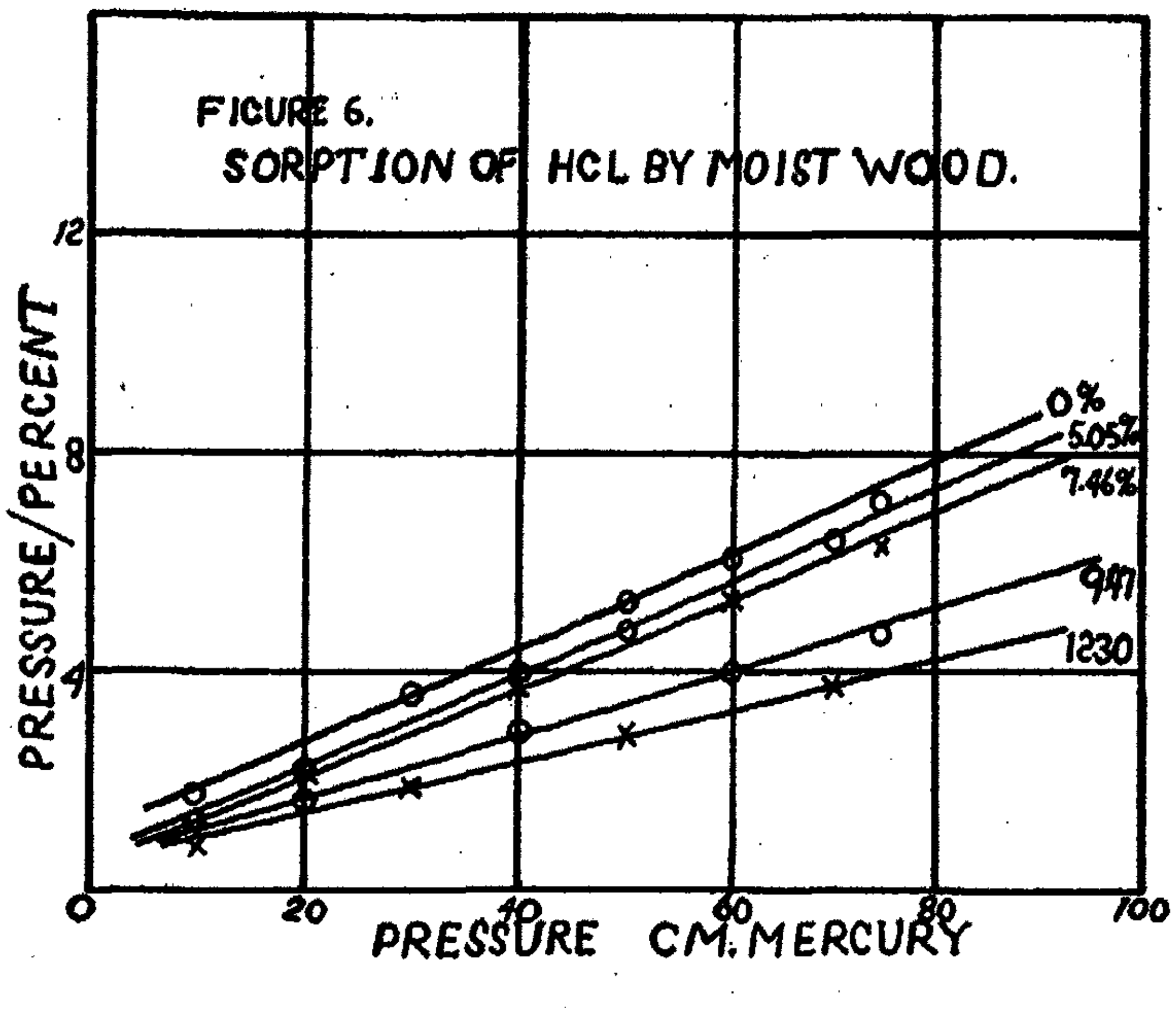
FIGURE 6.
SORPTION OF HCL BY MOIST WOOD.
PRESSURE/PERCENT
PRESSURE CM. MERCURY
0
4
8
12
20
40
60
80
100
0%
5.05%
7.46%
9.47
12.30

put to increased sorption of the wet samples (above 4% moisture content) is that the water increases the active surface of the cellulose, on which adsorption takes place. In that case the application of Langmuir's formula to the data of Table III should also give straight lines. Fig. 6 shows that this is the case. On each curve is indicated the percent of water. The only one not conforming to a straight line is the one just below 4% of sorbed water. The decrease in HCl sorption below 4% water content, can then be explained by the active surface being partially used up by the absorbed water. This effect will, of course, hold for all the other determinations, but is more than counterbalanced by the increase in active surface, caused by the addition of the larger amounts of water.

The decrease in sorption, when water is left by desorption, can also be explained. The water, so held, is more intimately associated with the cellulose, as is shown by the lower vapor pressure of the water desorption point. This results in a greater decrease of the active sorbing surface available for the HCl sorption.

The Sorption of Sulphur Dioxide, Ammonia and Carbon Dioxide by Wood and Cellulose

Cotton cellulose takes up sulphur dioxide exceedingly slowly, over 100 hours is required for the establishment of equilibrium. At a gas pressure of 76 cm and at 22°C approximately 5% is sorbed. The last 0.80% of this is held very rigidly, ordinary evacuation does not, over a period of 3 days, remove this part of the sorbed gas. However, 3 hours of heating at 85°C removed the last traces.

The sorption of sulphur dioxide evidently does effect some permanent alteration in the cellulose. The sorption values indicated above are not reproducible. The second sorption at an identical gas pressure gives a sorption value of 3.09% as compared to 5.10% initially determined. Further, a water vapor sorption was determined on this sample, and there results a slight change in sorption capacity, in the region of high relative humidities. There is an increase in sorptive power comparable to that found in the case of hydrogen chloride treated cellulose.

A characteristically different behavior is noted when wood is considered. Spruce sapwood alone has been investigated.

There is a much larger amount of sulphur dioxide taken up by the wood, than is the case with cotton, 13.6% as compared to 5%. Further, the time to reach the true equilibrium condition is comparatively small, 10 hours is the time interval at 76 cm pressure of the gas. Another marked difference is the much greater amount of the residual gas. After 24 hours evacuation nearly 4% of the sorbed sulphur dioxide is still held by the wood. This is, however, readily removed on heating to 85°C.

In general the results with ammonia are similar to those which have just been discussed. Approximately 4% of ammonia is sorbed by cotton cellulose at 76 cm pressure. Equilibrium takes roughly 48 hours. However, the sorbed gas is very easily removed, one hour on the vacuum effects its complete elimination.

As was the case with sulphur dioxide and wood, the latter takes up much more ammonia than does cotton. The equilibrium value is reached in about 12 hours, and indicates a sorption of 7.37% at 76 cm pressure of ammonia. All but the last 1% of the sorbed ammonia is quite easily removed on evacuation. However, even heating to 95°C still left a residue of 0.40%.

The work to date with sulphur dioxide and ammonia is merely introductory. However, even from such preliminary experiments, certain generalizations seem to be justified. With wood the attainment of equilibrium takes much less time than with pure cotton cellulose. The modifying influence of the non-cellulose constituents, as well perhaps, as its structure, evidently influence the sorbing system to a marked extent. Also the degree of sorption is quite different with the wood samples investigated. It is on a much larger scale.

Carbon dioxide is not appreciably sorbed by cellulose, up to a gas pressure of 76 cm. Further, if the cotton cellulose contains 5% of absorbed water there is still absolutely no sorption evident. With wood, 1.07% of sorption takes place at a pressure of 42 cm. Raising the pressure to 76 cm causes no increase in the amount of sorption. The sorbed gas is readily removed. Starting with 0 sorption and a pressure of 76 cm only 1.03% of carbon dioxide is sorbed. From 0 sorption and at 22 cm pressure, a sorption of 0.75% is observed. Apparently sorption becomes asymptotic to the value 1% somewhere between a gas pressure of 22 cm and 42 cm. If wood contains 3.36% of water, there is absolutely no sorption of carbon dioxide by such a sample. The water completely inhibits the appreciable retention of carbon dioxide.

The Sorption of Ethyl Ether, Amylene and Methyl Alcohol by White Spruce Heartwood

The investigation conducted with the above vapors has been merely introductory. However, it is felt that the results are of interest, and also, that further profitable lines of study may be indicated.

Sorption of Ethyl Ether.

The sorption took place at 22°C.

Equilibrium was reached, on the average, in about 12 hours.

% Sorption	Vapor Pressure (cm Hg)
0.53	10.20
0.69	19.60
1.16	38.20

The sorbed gas is readily and completely removed on evacuation.

These results indicate that there is very slight tendency for wood (white spruce heartwood) to take up ether, even when the relative vapor pressure approaches 90%. No work has been done on the sorption of this vapor by cotton cellulose. However, it is to be expected that the extent of sorption would be very slight as in the case of all the other vapors investigated to date, wood takes up considerably more than does cotton cellulose.

Sorption of Amylene.

At 10 cm pressure no appreciable sorption occurs, on raising the pressure to 25 cm a sorption of 0.47% is observed. Further increase of the vapor pressure until condensation took place (100% relative vapor pressure) resulted in an unchanged sorption. Thus, this unsaturated hydrocarbon is taken up to an even smaller extent than is ethyl ether.

The Sorption of Methyl Alcohol.

% Sorption	Time (minutes)	% Sorption	Time (minutes)
2.19	10	4.66	60
2.69	15	4.92	75
3.23	20	5.22	105
3.58	25	6.12	270
3.91	35	6.42	16 (hours)
4.10	45	6.42	18 "

(Final pressure 3.70 cm. Temperature 22°C)

Equilibrium Sorption Values

% Sorption	% Relative Vapor Pressure	% Sorption	% Relative Vapor Pressure
6.42	34.41	8.21	60.34
7.19	54.31	11.69	83.15
Equilibrium Desorption Values			
10.05	50	8.37	31
9.54	44	7.61	27

These results indicate quite clearly that the sorption of methyl alcohol by wood takes place on a relatively large scale. Also the fact of definite and marked hysteresis is very evident. Time has not permitted a detailed study of this system but the indications are that this will eventually prove to be an extremely interesting field, especially when comparisons are made with similar data to be obtained from cotton.

Discussion

As was indicated in the introduction, no revolutionary theories are to be drawn from the data which are presented above. However, in conclusion, a certain number of experimental facts are to be tabulated, followed by a working hypothesis whose main virtue may be looked on from the point of view of indicating the direction for further research.

Undoubtedly wood sorbs water vapor to a greater extent than cotton cellulose, and since Pidgeon and Maass have shown that this increase in sorption is not due to the lignin and as the experiments on extracted wood have shown this is not due to the extractible portion of the wood, it follows that the cellulose in the wood sorbs water to a greater extent than cotton cellulose and perhaps even to a greater extent than mercerized cotton. The sorption of water vapor in wood seems to be independent in large measure of the species and to be of the same order of magnitude for sap and heartwood. The comparative sorption experiments of various vapors on wood and cotton indicate that wood in every case sorbs a larger amount of vapor, and also, that in every case the steady state sorption value is obtained far more readily in wood than it is obtained in cotton.

The authors believe that the hypothesis advanced by Pierce[6] with regard to water vapor sorption is in the main correct. Water is sorbed in two ways; one involving a surface compound formation perhaps on the basis of one of water to one exposed hexose group, in the other the rest of the water is used to fill spaces available under attractive forces like those in a liquid. The volume change observed by Filby and Maass in the addition of the first bit of water is in agreement with the sorption of hydrogen chloride experiments described above. They indicate that this water loses its ordinary characteristics, and therefore, this water is to be regarded as directly combined. The experiments, however, seem to indicate that with increased sorption of water the surface available for such compound formation is also increased. Without regarding the following as a rigid way of presenting what happens, it is tentatively suggested that the cellulose micelles offer a certain free surface for this surface addition of water and that this surface is increased when actually liquid water fills the interstices at the edges of the micelles. At that point the competition of cellulose surface for cellulose surface goes into competition with that of cellulose surface for water. On this basis too the phenomenon of hysteresis is explainable. Originally, the cellulose surfaces being together, a certain amount of energy is required to displace them, before the water will take their place either partially or completely. Consequently, the amount of adsorption with continued increase in sorption of water vapor, lags behind a value which would be obtained were the micelle surfaces not acting upon one another. On desorption, that is with decreased concentration of water vapor, this hindrance has been removed, and the sorbed water has a greater value. It is tempting to go on to make further deductions, such as, that the cellulose in wood is in a much finer state of distribution, as far as the size of the micelles is concerned, corresponding somewhat to mercerized cotton. Such speculations, however, must be left until further work has been carried out.

The direction which further investigation should take is a comparison of sorption values of cellulose obtained from various sources. Especially, accurate determinations at the low relative humidity range are desirable. The heat liberated at various stages of water vapor sorption should be accurately measured. The experiments of Filby and Maass on water vapor sorption should be carried out with greater refinement over the whole sorption isotherm, both for adsorption and desorption. These researches are under way.

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[6] Shirley Institute Memoirs, 8, 35 (1929).

THE SORPTION OF SODIUM HYDROXIDE ON CELLULOSE AND WOOD

BY R. RICHARDSON* AND O. MAASS

This paper consists of data dealing with the effect of aqueous sodium hydroxide on cellulose, in particular with its sorption qualities. It is presented in the form of plates of some results obtained at the University of McGill.** In review, whereas cotton alkali sorption has been previously investigated, practically no results for wood cellulose are to be found in the literature. Wood cellulose was first used but it was natural to extend the measurements to other types of cellulose. In a practical way the related industries of mercerization, alkali cooking, and zanthating may make use of the results. Theoretically the subject is interesting from a standpoint of absorption in an abstract sense apart from the materials used. Since adsorption theory is in advance of absorption theory at presents experiments on absorption are particularly interesting.

The sorption calculations were made from measurements of the change in concentration of the liquid solution before and after contact with a known amount of the solid phase. For purposes of cursory investigation and of time factor determinations, conductometric measurements were satisfactory and flexible and were first used. For detailed work titrometric and occasionally gravimetric methods were used. The samples for titration were secured in a weight pipette. The accuracy in analysis attained was such that the average deviation from the mean was 1 part in 4000 at 40% alkali. Each determination of a concentration consisted of the average of 3 such analyses. Quantities were adjusted to produce a concentration change of 0.5%. The samples of cotton and "Celanese" were purified by cooking in a one percent alkali solution for 4 days. The purification of spruce was attempted as can be seen from one of the spruce plates. Plate number 9. The lignin is partially attacked, however, and results are not repeatable. The sample denoted as "Celanese" has suffered considerable alteration in purification and is not to be compared with the original commercial sample. The acetyl number of the purified "Celanese" is being estimated to determine the degree of alteration but this value is not yet available. A reaction period of 1 hour was agreed on for celanese above 45% where the downward trend of the curve for "Celanese" is due to the slow diffusion in such viscous solutions.

There is a strong temptation to present nothing but facts and results since it is certain that with further investigation the interpretations given to certain

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of the curves must be changed. Such a course would be, however, dull. It is particularily requested that the deductions made at this time concerning the results be regarded as purely working hypotheses. Final conclusions cannot yet be hazarded.

The use of the terms sorption, adsorption, and absorption are familiar enough. In this article sorption is a general term. Adsorption refers to surface concentration on a solid structure. Absorption refers to internal concentration throughout the solid structure. The use of such terms as pseudo sorption and others is not so general. Anticipating criticism from their use they will be explained in some detail. It is obviously not expressing the facts to say that in a 25% solution of alkali 0,2 g of NaOH is sorbed per gram of cotton since there must be some water sorbed or associated with the cotton contemporaneously. The hygroscopicity of cotton suggests that cotton in solution would not be bone dry. There must be two values, one for alkali and one for water, for example, 0.3 g NaOH plus 0.3 g H_2O. Such true values have never yet been accurately obtained. The value 0.2 g NaOH is all that can be measured. It is a net result of the two true values. To express this fact it is perhaps permissible to use the term pseudo sorption to be applied to such a result as 0.2 g NaOH. It will be argued that the term is unnecessary since the true values have never been determined. In rebuttal it may be pointed out that the literature abounds with citations of molecular ratios of compounds calculated from pseudo sorption curves by investigators who have not realized that such values are only useful by comparison and are not absolute in nature. The use of such a term would caution against the misuse of sorption values. This case is not the only example of errors contracted by the promiscuous use of sorption values. Consider the addition of salt to the solution of alkali. Until the sorption of any of the three liquid constituents is proved equal to zero it must be assumed that there is a true value for each, one for alkali, one for salt, and one for water. By analysing for alkali alone and considering mathematically that the salt is water a value is obtained which is denoted as the uni-pseudo sorption value of the alkali. However, by analysing for all three components, the net difference between the true values of alkali and the actual water alone can be calculated. In this manner the bi-pseudo sorption of the alkali is obtained. The literature records only uni-pseudo values whereas bi-pseudo values are much better indicators of the true state of affairs.

The mathematical definitions of these sorption terms are given.

Symbols.

a Bone dry weight of solid phase, gms.

b Weight of solution used, gms.

M Moisture content of the solid phase before the experiment, gms. H_2O per bone dry gm. of solid phase.

x, y, z, the original concentrations of alkali, salt, and water in the solution, % by weight.

x′, y′, z′, the final concentrations of alkali, salt, and water in the solution, % by weight.

Case 1.

Let there be two liquid phase components, alkali and water, and it be desired to calculate the alkali as sorbed. Then the water is considered as unsorbed.

Pseudo sorption of x (alkali).

$$\frac{b(x-x')-x'aM}{a(100-x')} \text{ g/g solid phase.}$$

Case 2.

Let there be three liquid phase components, alkali, salt, and water, and it be desired to calculate the alkali as sorbed, and let the water plus salt be considered as unsorbed.

Uni-pseudo sorption of x (alkali).

$$\frac{b(x-x')-x'aM}{a(100-x')} \text{ g/g solid phase.}$$

The similarity of form to case one explains in part why these values were first used in place of bi-pseudo results. Note that y and y′ need not be known.

Case 3.

Let there be three liquid phase components, alkali, salt, and water, and it be desired to calculate the alkali and salt as simultaneously sorbed. Then the water alone is considered as unsorbed.

Bi-pseudo sorption of x (alkali).

$$\frac{bxz'-bzx'-100aMx'}{100az'} \text{ g/g solid phase.}$$

Bi-pseudo sorption of y (salt).

$$\frac{byz'-bzy'-100aMy'}{100az'} \text{ g/g solid phase.}$$

Certain experimenters have erroneously considered M equal to zero. If M is small the error introduced is numerically small, as in the case of air-dry cotton. In other cases it cannot be ignored. The practice of neglecting M is likely to cause mistakes. Wood samples are usually presoaked in water so that equilibrium may be attained rapidly during the experiment and M in these cases is very large.

A factor due to the solution of the solid phase in the liquid phase is neglected in these formulae but is sometimes appreciable.

As a summary to these formulae and mathematical considerations it may be generalized that if there are n liquid phase components, having chosen one to be considered unsorbed (unless otherwise stated this is usually the solvent), n-1 simultaneous pseudo sorption values can be determined, one for each of the remaining liquid phase components. This is a much better procedure than choosing n-1 components to be unsorbed and calculating the sorption of the nth component, even if this operation be repeated until values for all components are obtained.

To illustrate these calculations and show that too much reliance must not be placed on uni-pseudo sorption values the boxed sorption values for sodium hydroxide in Plate 1 may be compared. The addition of the salt has increased the sorption of alkali but the bi-pseudo sorption value shows that the increase is really not as large as would be concluded from the uni-pseudo value. The prefixes uni and bi refer to the number of liquid phase components which the mathematical procedure in each case permits having a simultaneous pseudo sorption value.

The above discussion shows that the results which will be given in the following tables can be relied on only to give the relative changes of sorption caused by a change in the concentration of the alkali or due to a different sample of cellulose. These results cannot be used in their present form and in the light of present knowledge to calculate stoichiometric proportions, etc. While it is sometimes possible to conclude that compounds are formed it is impossible to calculate their formulae.

In the authors' opinion no reliable and complete data for sorption of NaOH on cotton exists at concentrations above 30%. It was found that only when

Plate 1

Spruce Flake Sorption

One hour, 20°C, in sodium hydroxide, salt, water systems

(A) Without salt.

Equilibrium solution % NaOH	Pseudo sorption g NaOH/bonedry g
4.562	0.0474
4.570	0.0353
4.348	0.0411
4.465	0.0397
4.508	0.0399
Average—	
4.591	0.0407

And by comparison with known adsorption values for another spruce sample:

3.9*	$\boxed{0.038}$

(B) With salt.

Equilibrium solution %NaOH—%NaCl		Uni-pseudo sorption g NaOH—g NaCl /bone dry g		Bi-pseudo sorption g NaOH—g NaCl /bone dry g	
3.837	9.705	0.0480	0.0382	0.0505	0.0428
3.899	9.625	0.0510	−0.0402	0.0498	−0.0337
3.850	9.625	0.0546	−0.0556	0.0528	−0.0504
3.898	9.713	0.0513	−0.0430	0.0497	−0.0346
3.920	9.148	0.0568	−0.0511	0.0551	−0.0471
Average of last four tests—					
3.9*	9.5	$\boxed{0.053}$	−0.048	$\boxed{0.042}$	−0.042

* Comparable values.

experimental determinations of the highest accuracy were made that reproducible results were possible. At high concentrations equilibrium is attained very slowly and with great experimental difficulty. Below 30% the data in the literature was used. Plate 2 illustrates the cotton isotherm at room temperature. Rumbold's[1] very intensive examination at low concentrations has been linked by the work of Vieweg[2] to the present examination of high concentrations. The curve is generally interpreted as being a combined effect of solid solution (adsorption) and of compound formation, the latter indicated by the horizontal reaches. At low concentrations the cotton curve is in sharp contrast with the curves for wood and "Celanese." The latter curves obey Freundlich's adsorption law. If the cotton curve is considered to be concave then the wood and "Celanese" curves are convex below ten per cent sodium hydroxide. The theory of the cotton curve is based on applications of the phase rule. Dalton's law of partial pressures may also be applied. In Nernst's Theoretical Chemistry it is cited as Dalton's law of absorption and as such applies to the absorption of gases in liquids. In this case it is extended to the distribution of alkali between the liquid solution (water) and the solid solution (cotton). Except for aberrations from the laws of ideal solutions a straight line relationship between sorption and concentration would indicate absorption. This rule for absorption takes the place of Freundlich's relation

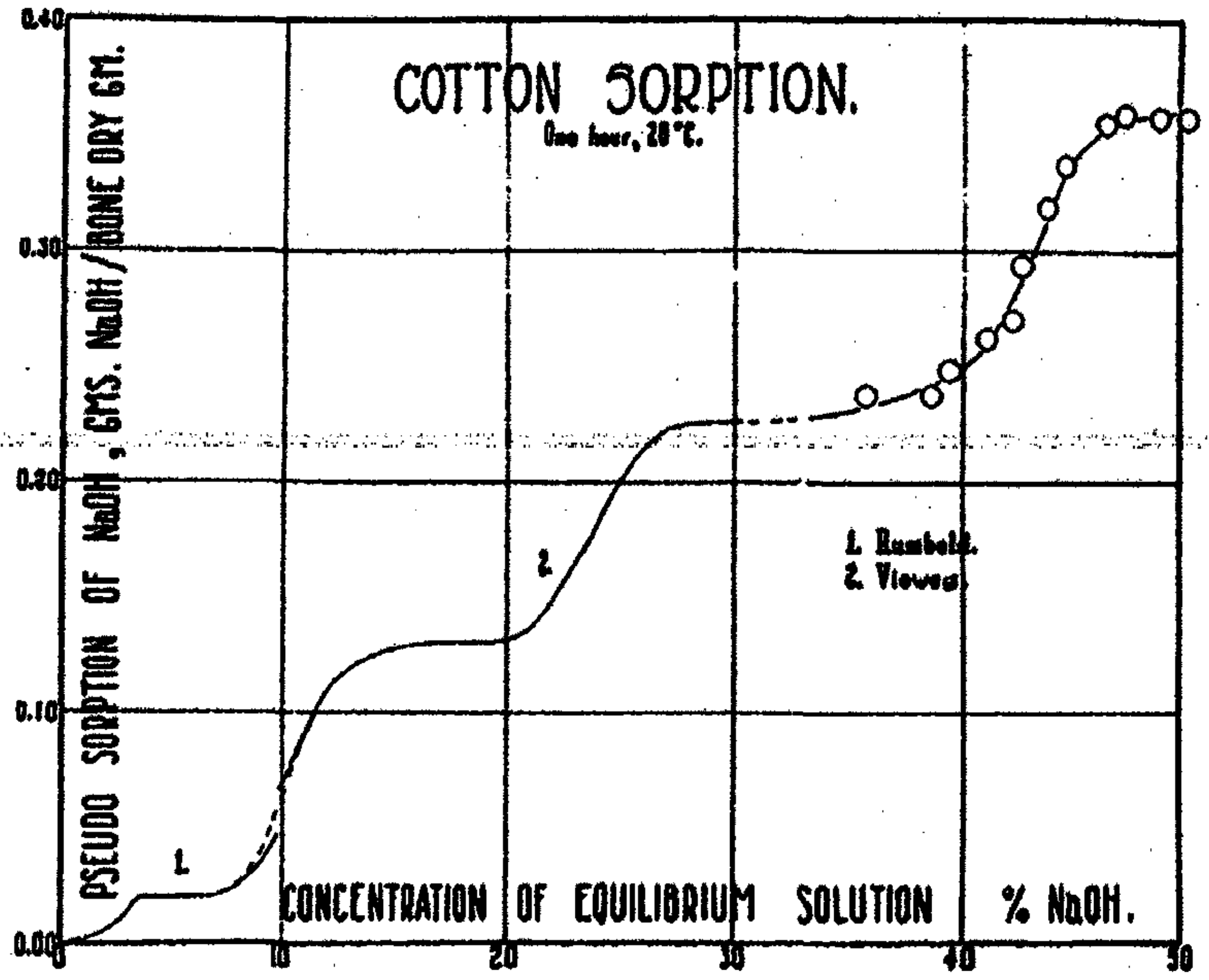

PLATE 2

Rumbold and Vieweg's values were not determined at one hour and 20°C but are nevertheless comparable with the determinations as shown by the circles; equilibrium in these cases being attained after very short time intervals.

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[1] J. Am. Chem. Soc., 52, 1013 (1930).

[2] Ber., 40, 3876 (1907).

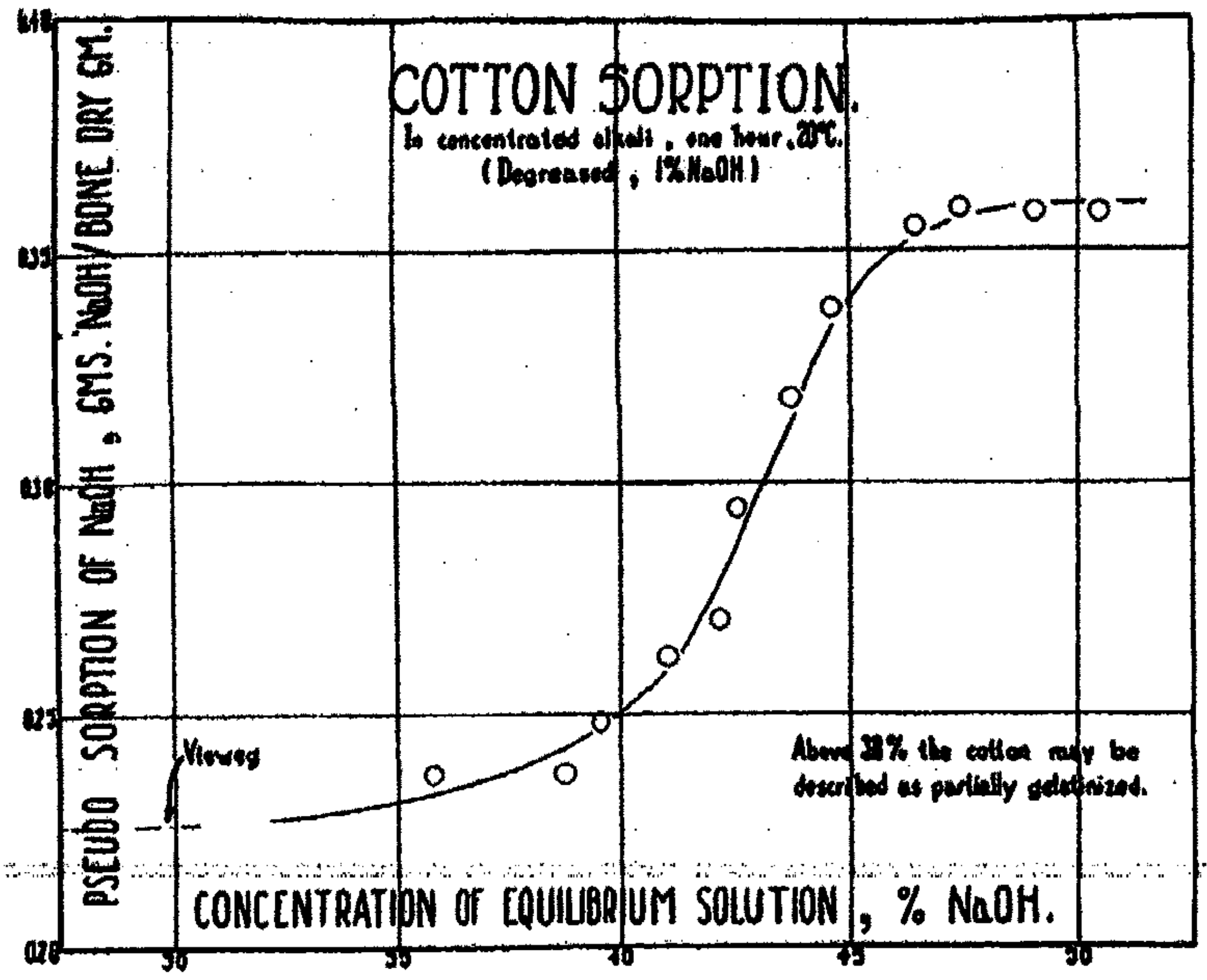

Plate 3

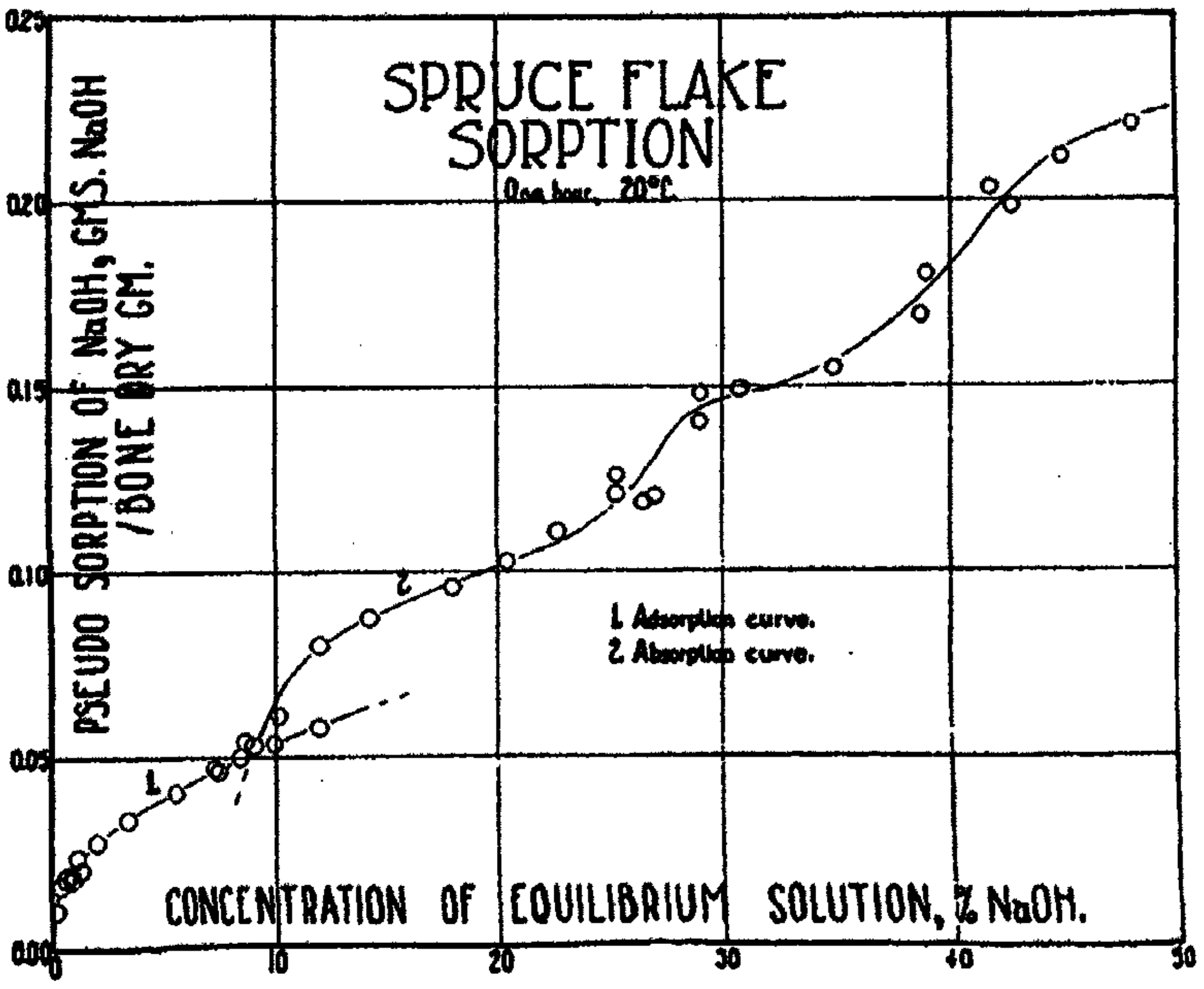

Plate 4

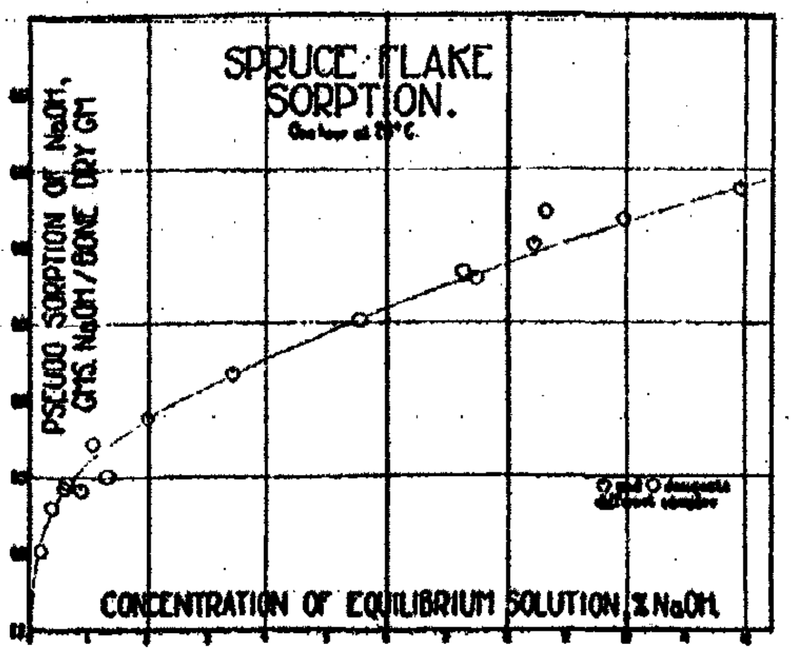

Plate 5

for adsorption. The phase rule indicates the same general type of curve for absorption as Dalton's law. If compounds are formed the phase rule predicts a step-like diagram. Experimentally the cotton curve appears to be a mean. Perhaps this may be considered somewhat similar in type to the Pd-H_2 sorption curve.

The term solid solution is here used as a partial synonym for absorption, to forcibly denote that the effect is internal in nature and to recall simultaneously that the curves have some theoretical basis in the phase rule and Dalton's law. The other laws of solid solutions may or may not be observed. It will require further work to settle these points. The precise configuration of alkali

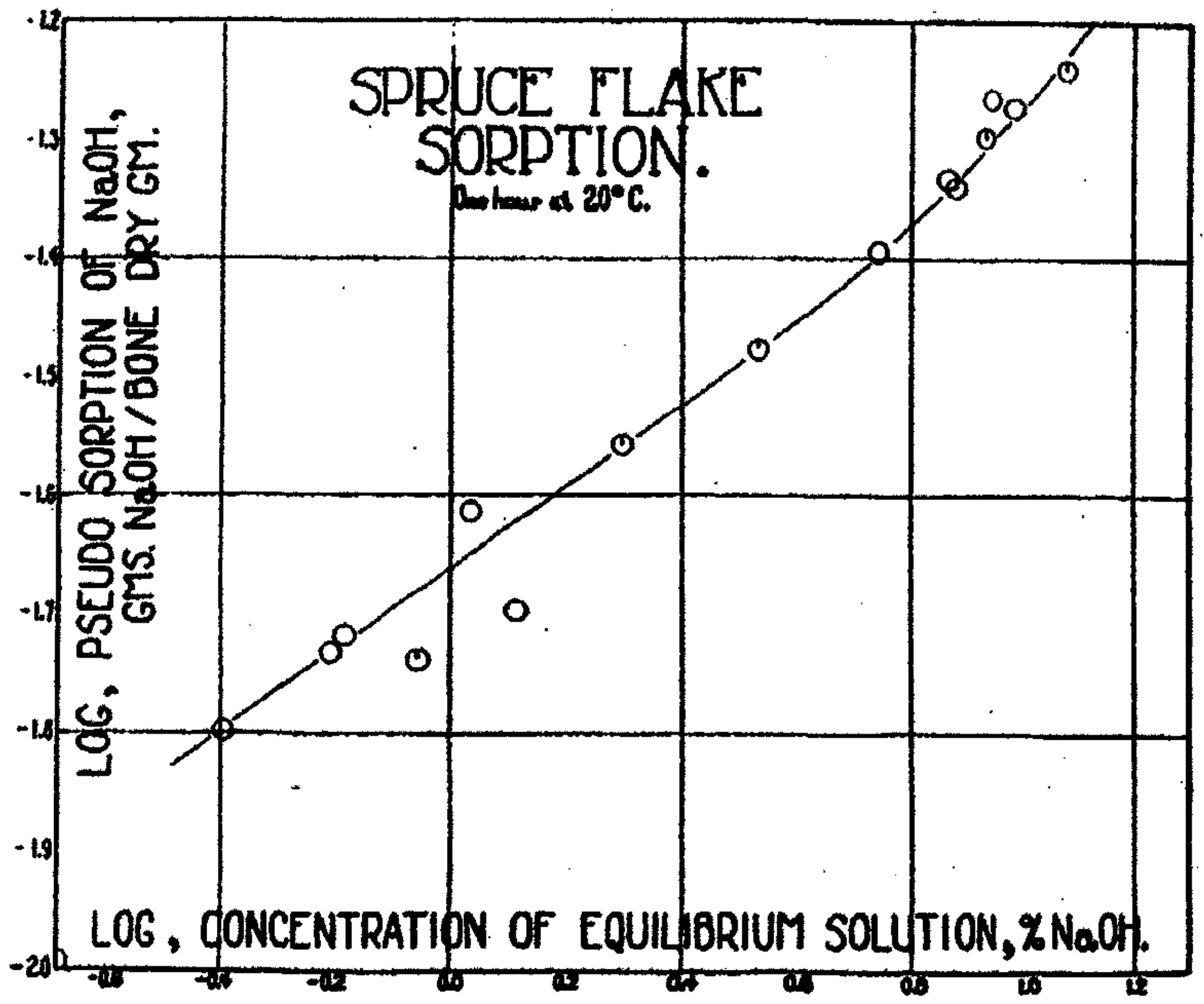

Plate 6

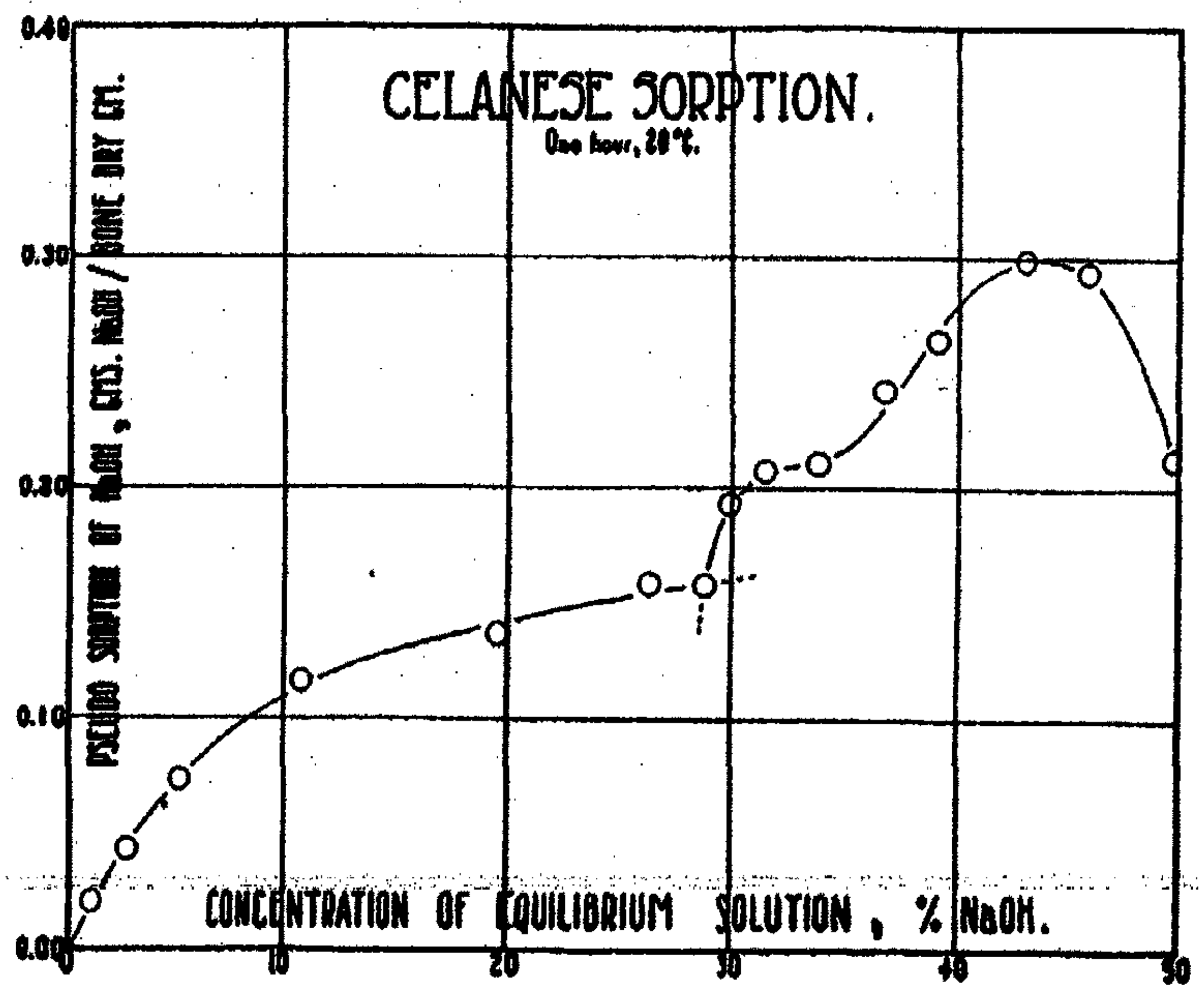

Plate 7

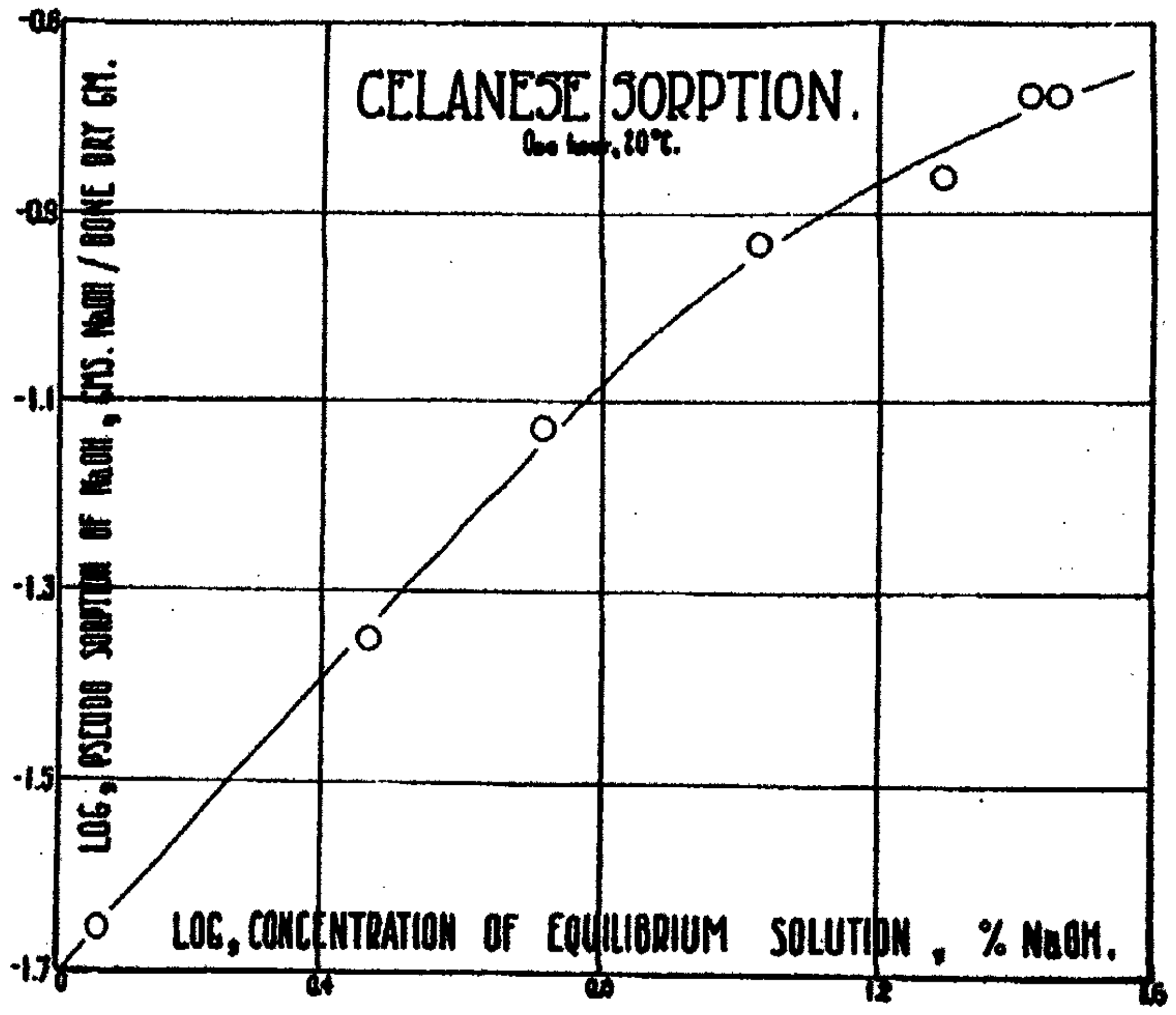

Plate 8

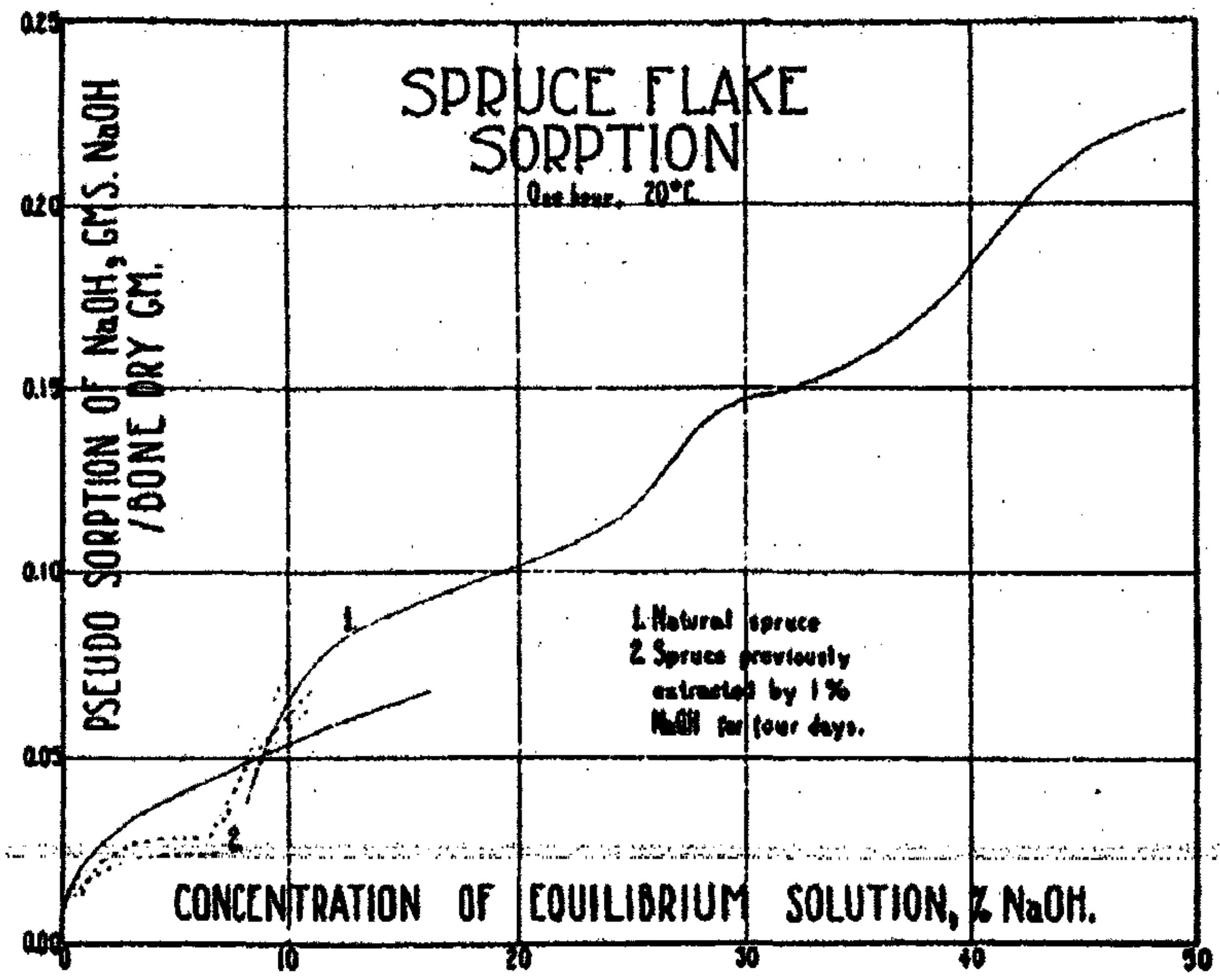

PLATE 9

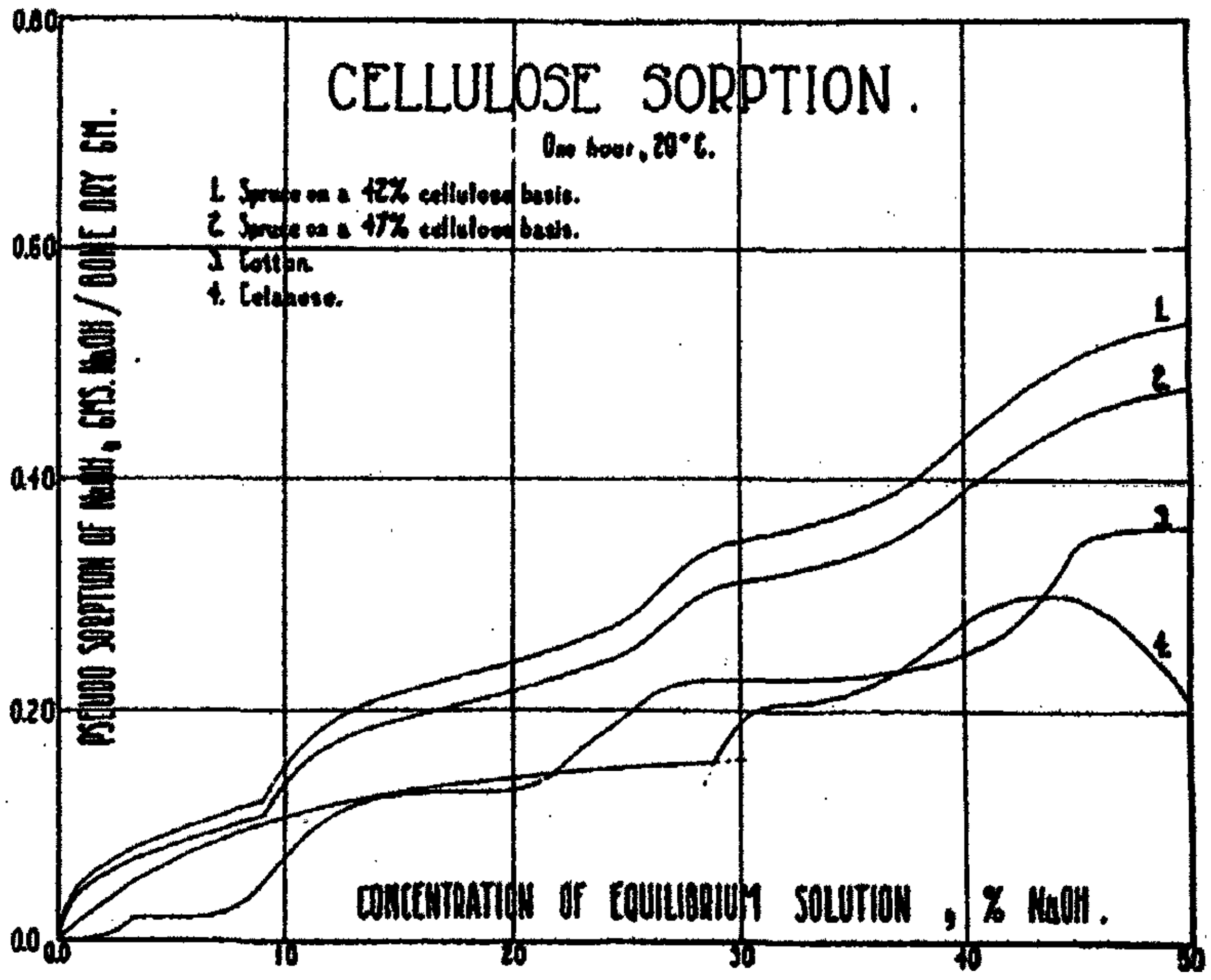

PLATE 10

and water in the cellulose crystal is not suggested. The term internal concentration may be substituted, or the original term absorption even may be considered of sufficient strength. A lucid portrayal of facts is desired more than anything else. Suggestions of more appropriate terms would be welcomed.

It should not be forgotten that the generally accepted explanation of the horizontal portions of the step-like cotton diagram as being due to compound formation may be entirely fallacious. The step-like diagram may be possibly due to a greater adsorbing area being produced by swelling actions occurring at critical concentrations. This viewpoint would eliminate absorption and attribute all curves to the effect of adsorption but on varying surface areas.

The remaining plates show the effect of the source of the cellulose on the sorption curves. Below approximately 10% for wood and 30% for "Celanese" the type of curve obtained is likely due to adsorption. These curves obey Freundlich's adsorption isotherm as shown by the straight line logarithmic plots of these curves below the critical concentrations just named. Plates number 6 and 8.

Work on cellophane is progressing. It is planned to complete this curve and obtain curves for rayon and viscose silk from cotton. The cotton curve at intermediate concentrations is to be reconsidered especially with regard to purified samples of various origins. When this work is finished it is hoped the interpretations of the curves will be more conclusive.

The planned work would include desorption measurement. A few of these have been made already.

It should be pointed out from Plate 10 that all these curves can be approximately represented by straight lines.

Each curve can be replaced by one straight line as a first approximation. The constant sorption differentials or tangents of each of these lines are given.

Spruce, on a basis of 44.5 % cellulose
= 0.010 g NaOH per g cellulose per % of conc. change in the solution
Cotton
= 0.070 g " cellulose " "
Celanese
= 0.066 g " " " "
Spruce, on a basis of total wood content
= 0.048 g NaOH per g wood per % of conc. change.

These relations may eventually evolve a substantial theory.

Various theories of adsorption and combination have been put forward by many workers in this field to explain alkali-cellulose affinity. Which name adsorption or combination is applied to this affinity is of little import as these terms merge into each other. The effect dealt with is certainly on the border line.

When this work is finished it is hoped the interpretation of the curves will be more conclusive.

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THE DECOMPOSITION OF DIMETHYL ETHER ON THE SURFACE OF PLATINUM

BY E. W. R. STEACIE AND H. A. REEVE

Introduction

It is of considerable interest to compare the velocities of homogeneous and heterogeneous gas reactions. In this connection it has been shown by Hinshelwood that there is a general tendency for homogeneous bimolecular reactions to become unimolecular on the surface of a catalyst, the heat of activation of the reaction falling to about one-half of its former value. This change in the characteristics of the reaction is accompanied by a modification of the reaction path.

The homogeneous decomposition of hydrogen iodide, for example, proceeds as indicated by the equation

$$2\ HI = H_2 + I_2.$$

The possible homogeneous unimolecular decomposition

$$HI = H + I,$$

followed by a subsequent recombination of the atoms, is ruled out since the formation of atomic hydrogen would be a highly endothermic process. The momentary concentration of a large amount of energy in the molecule would thus be necessary, and hence a very large heat of activation would be associated with the reaction. The presence of a metal surface, however, renders such a change possible since the atomic hydrogen and iodine formed can be held on the surface in an adsorbed condition, and later the atoms evaporate in pairs as molecular hydrogen and iodine.

The heat of activation of the homogeneous bimolecular decomposition is 44,000 calories per gram molecule.[1] In order that two molecules may decompose, they must therefore have a combined energy in excess of 44,000 calories. For the heterogeneous unimolecular decomposition on the surface of gold the heat of activation is 25,000 calories.[2] Hence one molecule in order to decompose must have an energy in excess of 25,000 calories. The lowering of the activation energy by the catalyst is therefore accompanied by a change in the mechanism of the reaction, in the one case only a single molecule being activated, while in the other case two molecules must be activated simultaneously. In consequence the effect of the catalyst on the magnitude of the activation energy is left unanswered.

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[1] Bodenstein: Z. physik. Chem., **29**, 295 (1899).

[2] Hinshelwood: J. Chem. Soc., **127**, 1552 (1925).

It is therefore of interest to compare the homogeneous and heterogeneous reactions in the case of a substance which decomposes homogeneously in a unimolecular manner. Previous investigations of this kind have been made with acetone,[3] ethyl ether,[4] and propionaldehyde.[5] The present paper deals with a similar investigation using methyl ether on the surface of platinum.

Methods of investigating Heterogeneous Gas Reactions. There are two main methods of investigating heterogeneous gas reactions.

(a) The catalyst is contained in a bulb in finely divided form. The reactant, or reactants, is admitted to the bulb, or passed through it continuously, and the reaction is followed by the pressure change which accompanies it or by analysis. This method is the simpler of the two, and is the more usual when the course of the reaction, yield, etc., is of primary importance. On account of the lack of definite knowledge of the surface, etc. it is not a suitable method of investigating the molecular statistics of the reaction.

(b) The catalyst consists of a fine filament stretched axially through the reaction vessel. The vessel containing the gas is kept at or near room temperature, while the filament is heated electrically to the desired temperature. This method is by far the most suitable when an accurate knowledge of the molecular statistics of the reaction is desired, and is the one used in this case. In this method the solid material can function in two ways, either by adsorbing the reactant and permitting a catalytic reaction, or else by merely acting as a source of energy. In the latter case the question of energy transfer between gas molecules and the solid surface will be of paramount importance.

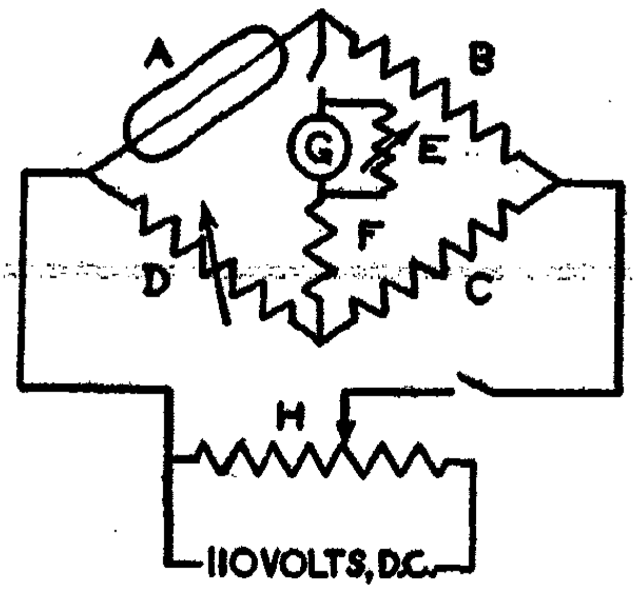

Fig. 1
Electrical Diagram

Apparatus. The apparatus was similar, with the exception of the electrical set-up, to that used in previous investigations. It consisted of a reaction bulb of about 100 cc capacity, through which a platinum wire (0.05 to 0.10 mm diameter) was sealed axially. The bulb was connected by capillary tubing and stopcocks to a capillary manometer, a supply of methyl ether, and a pumping system. The connecting tubing was wound with nichrome wire and heated electrically to prevent condensation. The reaction bulb was immersed in an oil bath, which was maintained at 45°C.

Temperature Measurement and Control. The temperature of the heated filament was obtained from its resistance in the following manner. The filament *A* (Fig. 1) was made one arm of a Wheatstone Bridge *ABCD*. Since

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[3] Taylor: J. Phys. Chem., 33, 1793 (1929).

[4] Steacie and Campbell: Proc. Roy. Soc., 128 A, 451 (1930); Taylor and Schwartz: J. Phys. Chem., 35, 1044 (1931).

[5] Steacie and Morton: Can. J. Research, 4, 582 (1931).

the resistance of the various filaments used was low (from 1 to 15 ohms), the standard resistance *B* was of the same magnitude and was immersed in a large, well-stirred oil-bath. The heating of this resistance was negligible with the current used. Two high resistances, *C* and *D*, were used in the other arm of the bridge. *C* was a standard 10,000 ohm resistance, and *D* was a variable 1/10 to 100,000 ohm, resistance.

A sensitive galvanometer, *G*, was used. The sensitivity could be varied by the resistance *F* in series, or by the variable shunt *E*. The voltage applied to the bridge was regulated by the potentiometer *H*, which was connected directly to the 110 volt D.C. supply.

Methyl ether[6] was prepared from sulphuric acid and methyl alcohol. The gas was bubbled through sulphuric acid saturated with methyl ether, passed through phosphorus pentoxide tubes, and fractionally distilled. During the course of the experiments it was stored as a liquid in a bulb immersed in a solid carbon dioxide-acetone mixture.

Experimental Procedure

The resistance of the filament was measured at various temperatures, as determined by a Leeds and Northrup optical pyrometer, over a range from 700° to 1100°C, at 50° intervals. A resistance-temperature curve was constructed from these results. On extrapolation this curve gave good agreement with the experimentally determined resistance at room temperature. Even if the absolute values of the temperature of the filament are slightly in error, this will be unimportant for the present purpose provided that the relative temperatures are in good agreement.

During any one run the bridge setting was such that a balance gave a filament resistance corresponding to the temperature desired. On account of the changing thermal conductivity of the gas mixtures, as the reaction progressed, it was necessary to vary the impressed voltage so as to maintain a balance in the bridge circuit.

The reaction was followed by admitting methyl ether to the reaction vessel, maintaining the filament at the desired temperature, and observing the variation of pressure with time.

The Course of the Reaction. Hinshelwood and Askey[7] found that the homogeneous decomposition of methyl ether was mainly as represented by the equation

$$\begin{aligned} CH_3OCH_3 &= [CH_4 + HCHO] \\ &= CH_4 + H_2 + CO. \end{aligned}$$

Thus in a typical analysis of the products they found 32.0% carbon monoxide, 33.5% hydrogen, and 34.5% methane.

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[6] We are indebted to Mr. J. S. Tapp of this laboratory for supplying the methyl ether used.

[7] Proc. Roy. Soc., 115 A, 215 (1927).

In the present investigation analysis showed that the reaction was, in the main, the same as the above. Thus a typical analysis at 977°C gave the following result: CO = 34.6%, CH_4 = 33.0%, H_2 = 32.5%.

In the homogeneous reaction, in agreement with the foregoing equation, pressure increases at completion of about 200% were obtained at all temperatures. In this investigation, however, pressure increases at completion of 186 ± 2% were invariably obtained. This somewhat lower value was undoubtedly due to the condensation of a small amount of paraformaldehyde on the walls of the reaction vessel. Since the final pressure increase was the same at all temperatures, however, it is justifiable to use the pressure increase as a criterion of the extent to which the reaction has progressed. The times for various fractional pressure increases have therefore been used as a measure of the reaction velocity.

Experimental Results

During the course of the investigation a number of different filaments were used. In general these filaments showed considerable differences on account of differing diameter, surface conditions, etc. In the case of a particular filament, after a certain amount of preliminary aging, a steady condition was finally reached and reproducible reaction velocity results could then be obtained. This steady condition might be upset, however, by too drastic heating.

The results given below were obtained on various filaments which had reached a steady condition. In any particular series the runs were made in random order to obviate any error due to aging.

The Effect of Pressure. Fig. 2 shows typical pressure-time curves for various initial pressures at 1150°K, on filament No. 1. The complete data for a typical run are given in Table I.

TABLE I

Filament No. 1. 1150°K

Time mins.	Pressure mm	Per cent decomposed	K
0	316	—	—
3	345	6.0	0.0194
8	412	17.4	0.0239
12	463	26.0	0.0250
17	520	35.8	0.0261
22	568	43.9	0.0262
29	624	53.4	0.0262
35	663	60.0	0.0262
40	692	65.1	0.0264
50	735	72.3	0.0258
60	766	77.5	0.0250

The values of per cent decomposition are calculated on the assumption that an increase in pressure of 186% corresponds to complete decomposition. The constants given in the last column are those calculated for a unimolecular reaction. As in the homogeneous reaction the constants rise in the early stages of the reaction while formaldehyde is accumulating, and finally become constant within the experimental error.

The effect of pressure on the rate of reaction is indicated by Fig. 3 and some typical data are given in Table II. As in the homogeneous reaction the velocity constants fall off at pressures below 300-400 mm.

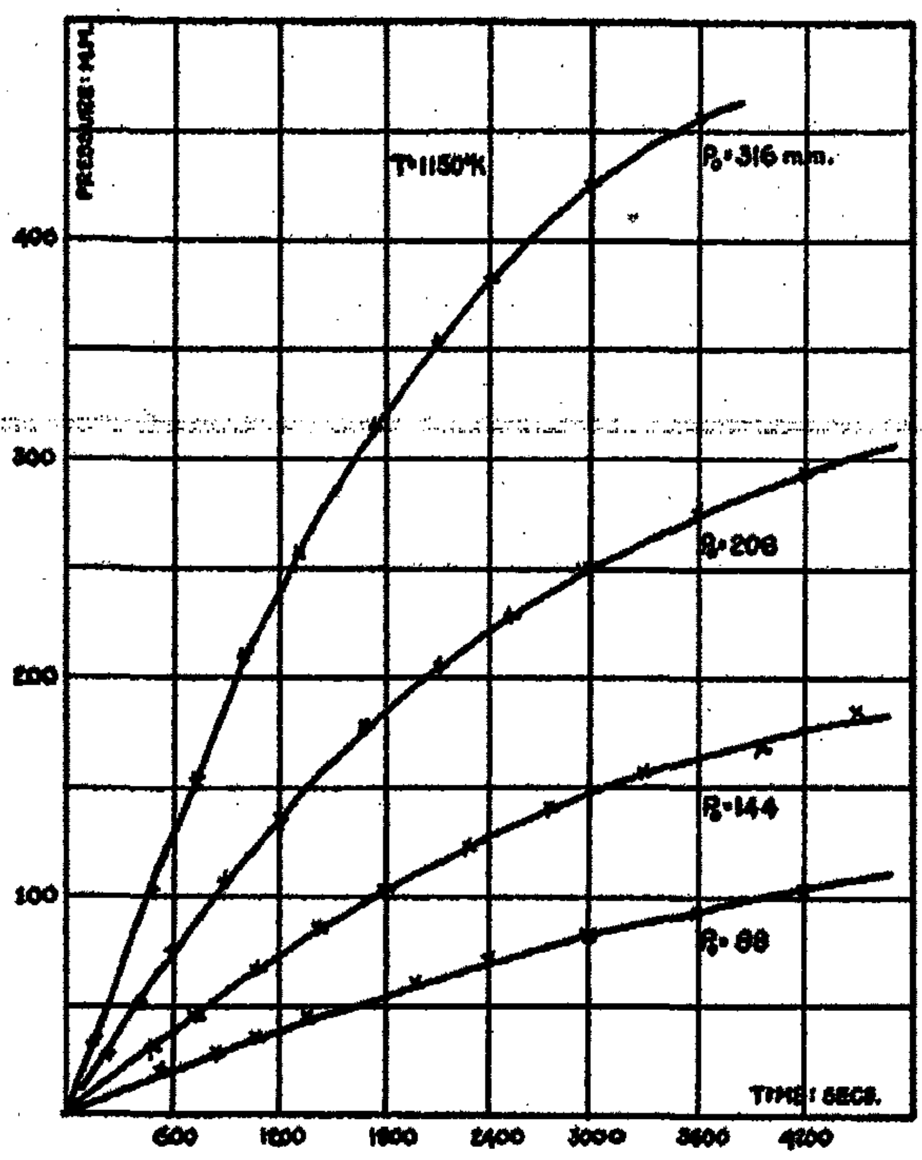

Fig. 2

Pressure-Time Curves

Table II

Filament No. 1

Temperature = 1150°K

Pressure mm	T_{50} mins.	T_{100} mins.	Pressure mm	T_{50} mins.	T_{100} mins.
97	23.0	53.6	316	12.0	29.0
98	25.5	64.4	318	12.0	28.3
144	19.3	48.4	430	10.0	23.0
206	14.3	35.3	432	10.7	25.4
314	10.6	25.4	433	10.7	25.4
315	12.6	30.0			

The Temperature Coefficient. The heat of activation was calculated from two entirely separate series of results on different filaments.

In the first series, for experimental reasons, it was impossible to use initial pressures above 400 mm. The heat of activation was therefore calculated by extrapolating the results at each temperature to the high pressure rate.

In the second series of results runs were made at initial pressures of about 700 mm. At these pressures the falling off was negligible and no extrapolation was necessary.

Some typical data for the second series are given in Table III. Fig. 4 shows a plot of log T_{25}, log T_{50} and log T_{100} against the reciprocal of the absolute temperature.

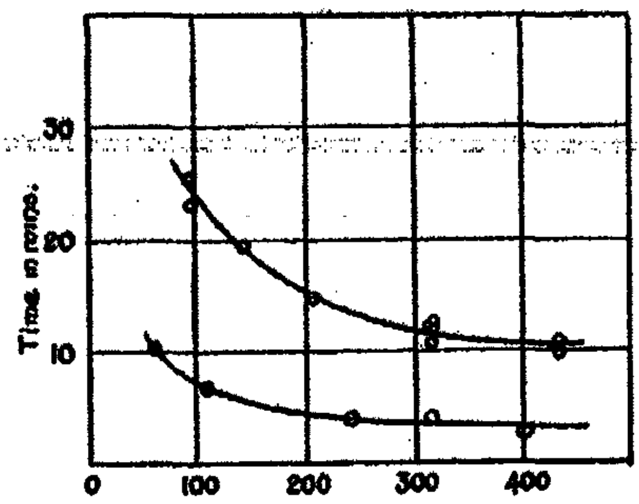

FIG. 3

The Effect of Pressure on the Rate of Reaction

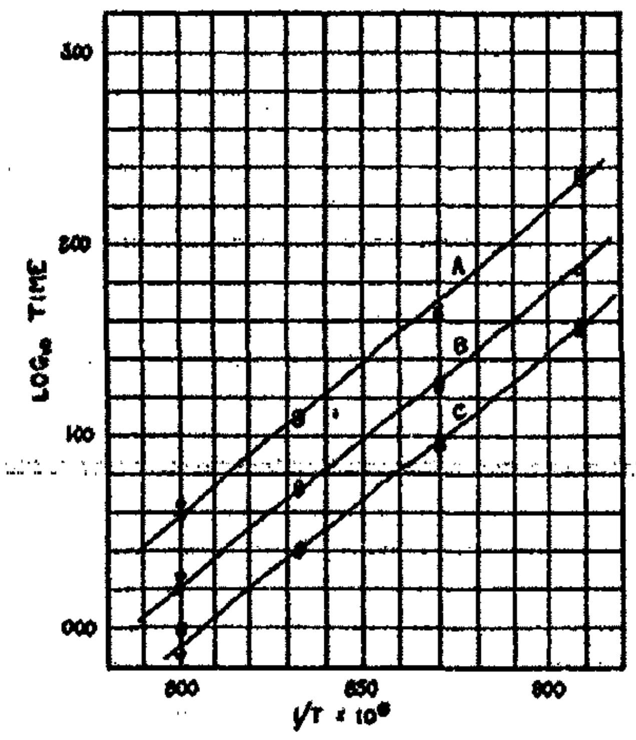

FIG. 4

The Temperature Coefficient

Curve A—Calculated from T_{100}

Curve B—Calculated from T_{50}

Curve C—Calculated from T_{25}

TABLE III

Filament No. 2

Initial pressures ca. 700 mm.

Temperature °K	T_{25} mins.	T_{50} mins.	T_{100} mins.
1100	37.5	74	216
	37.0	74	236
1150	8.75	17.8	43
	9.25	18.5	47
1200	2.53	5.20	12.2
	2.58	5.33	12.5
1250	0.92	1.60	3.84
	0.97	1.87	4.33
	0.73		

The heats of activation calculated for various fractional times for both series of results are given in Table IV.

TABLE IV

Series	Heat of Activation		
	from T_{25}	from T_{50}	from T_{100}
		calories per gram mol.	
1	—	68500	70100
2	68300	69500	72200

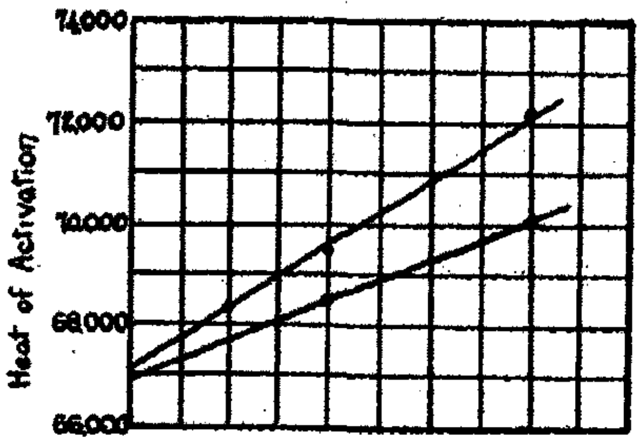

FIG. 5

Extrapolation of the Heat of Activation to Initial Rates

On account of the complication due to the intermediate formation of formaldehyde, the best values of the heat of activation will be obtained by the extrapolation of the above values to initial rates. This is done in Fig. 5. The values obtained in this way for the two series are 66900 and 67100 calories. The mean value of the heat of activation is therefore 67000, as compared with 58500 found by Hinshelwood and Askey for the homogeneous reaction.

Discussion

A comparison of the heats of activation of homogeneous unimolecular decompositions with those of the same reactions in contact with hot filaments shows that the results fall into two classes. The data are summarized in Table V.

TABLE V

Substance	Heat of Activation	
	Homogeneous	Filament
Acetone	68,500	68,400
Ethyl Ether		
(Steacie & Campbell)	53,000	52,000
(Taylor & Schwartz)		57,000
Propionaldehyde	55,000	96,500
Methyl Ether	58,500	67,000

It will be seen that in the first two cases the heats of activation agree within the experimental error, while in the last two the heat of activation of the filament reaction is *higher* than that of the homogeneous reaction. This point will be discussed later in detail.

There are two possible explanations of the action of the filament in these reactions: (a) Molecules are activated by collisions with the filament, statistical redistribution of energy being produced by such collisions. (b) The filament serves as a source of energy, the surrounding gas layer being maintained at a high temperature. Activation takes place in the hot gas layer by ordinary molecular collisions.

The second explanation seems by far the more likely, since it is difficult to see why the velocity constants should fall off at low pressures if collision with the filament were a necessary preliminary to reaction. That this is the correct explanation may be proved conclusively by an examination of the statistics of the reaction.

Some typical data for the decomposition of methyl ether in contact with platinum follow: Filament temperature, 1150°K; pressure, 316 mm; volume of reaction vessel, 100 cc; filament length, 10 cm; filament diameter, 0.06 mm; bath temperature, 318°K; rate of decomposition, 0.033% per sec. Whence we obtain: (*a*) *The number of molecules reacting* which is 3.19×10^{17} molecules per sec. and (*b*) *The number of molecules hitting the filament.*

According to Knudsen's equation we have

$$m = \sqrt{\frac{M}{2\pi RT}}p,$$

where m is the mass of gas striking the filament per sq. cm. per second, M is the molecular weight, T is the absolute temperature, and p is the pressure in bars. Evaluating the constants, and putting the pressure in atmospheres, we have

$$m = 44.2\sqrt{M/T}\,p.$$

The value of T to be used is somewhat uncertain. Since we are only interested in the order of magnitude of the results, it is not of much importance, and the simplest assumption to make is that the temperature of the colliding molecules is that of the filament. In any case an error of even 200° in T will not introduce more than a 10% error into the result.

Whence we have $m = 3.68$ g per sec. per sq. cm., hence the number of molecules striking the filament is 4.85×10^{22} molecules per sq. cm. per sec. The surface area of the filament is 0.188 sq. cm., hence we have *number of molecules striking the filament* $= 9.12 \times 10^{21}$ per second.

(*c*) *The fraction of the molecules at 1150°K possessing the energy of activation.*

Using Hinshelwood's form of theory, this will be given by

$$\frac{e^{-\frac{E+(\frac{1}{2}n-1)RT}{RT}}\left(\frac{E+(\frac{1}{2}n-1)RT}{RT}\right)^{\frac{1}{2}n-1}}{\underline{\left|\tfrac{1}{2}n-1\right.}}$$

Assuming that the heat of activation found by Hinshelwood and Askey for the homogeneous reaction is the true one, we have $E = 58500$, and $n =$ ca. 12. Whence the fraction of the molecules at 1150°K which possess the energy of activation $= 1.36 \times 10^{-8}$. Hence the total number of activated molecules, produced by collisions with the filament only is $9.12 \times 10^{21} \times 1.36 \times 10^{-8} = 1.24 \times 10^{14}$ molecules per sec.

Hence about 2600 molecules react for every one which obtains the necessary energy from the filament by direct collision. It may therefore be concluded that the reaction is occurring in a layer of hot gas surrounding the filament. The effective dimensions of this layer may be calculated as follows:

The total number of molecules entering into collisions in the gas per cc per sec. is given by

$$2\sqrt{2}\,\pi s^2 un^2,$$

where s is the molecular diameter, *u* the root mean square velocity, and *n* the number of molecules per cc. The total number of activated molecules produced in the gas per cc per sec. is therefore given by

$$\frac{2\sqrt{2}\,\pi s^2un^2e^{-\frac{E + (\frac{1}{2}n - 1)RT}{RT}}\left(\frac{E + (\frac{1}{2}n - 1)RT}{RT}\right)^{\frac{1}{2}n-1}}{\underline{|\tfrac{1}{2}n - 1}}$$

In order to evaluate this expression it is necessary to assign a value to *s*, the molecular diameter. Kinetic theory considerations indicate a value of about 5×10^{-8} cm. It is known, however, that molecules with a high energy content can transfer energy by resonance, and in general in dealing with energy transfers effective diameters much larger than kinetic theory diameters must be used. We may therefore assume $S = 20 \times 10^{-8}$ cm. Whence the number of activated molecules produced by collisions in the gas at 1150°K is 3.54×10^{22} molecules per cc per sec.

The number of molecules reacting per second is 3.19×10^{17}. Hence the effective volume of the space in which reaction occurs is

$$\frac{3.19 \times 10^{17}}{3.54 \times 10^{22}} = 9.00 \times 10^{-6}\text{ cc}$$

Whence the effective thickness of the region surrounding the filament in which reaction occurs is 4.73×10^{-4} mm.[*]

It is well known that practically the entire temperature drop in the gas surrounding a filament of this type takes place in a "skin" about 0.5 mm thick by conduction. The last few degrees drop is much more gradual, and the heat transfer takes place mainly by convection. The total temperature drop here is 832°. If we assume that 750° of this occurs in such a layer, then the reaction is occurring in a zone surrounding the wire which includes a temperature gradient of about 1°. The volume, however, is a minimum value, as explained before. We may therefore conclude that the zone in which reaction occurs does not include a great enough temperature gradient to introduce any appreciable error into the calculated value of the temperature coefficient of the reaction, *provided that the filament is in thermal equilibrium with the gas.*

Calculations for ethyl ether, acetone, and propionaldehyde yield similar results. In every case it is necessary to assume that the reaction occurs in a hot gas layer surrounding the filament.

We may therefore consider that the dynamics of the decomposition of ethyl ether and of acetone are completely explained. In the case of propional-

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[*] Since this volume is obtained by equating the number of molecules activated to the number reacting, it will be a minimum value. It will, however, be approximately correct since the calculations have been made for a pressure at which the velocity constants have fallen off to an appreciable extent.

dehyde and of methyl ether, however, it is still necessary to explain the fact that the temperature coefficients are higher than those of the homogeneous reactions. The heats of activation calculated for the filament reactions cannot be the true ones. Thus for propionaldehyde calculation shows that if the true value of E were 96,500 calories, then even if the whole reaction vessel were at the temperature of the filament the rate would still be 167 times slower than the observed value.

The only possible explanation of the high temperature coefficients of these reactions would seem to involve the transfer of energy between the filament and incident gas molecules.

Energy Transfer between Gas Molecules and the Filament. By means of heat conductivity measurements at low pressures Soddy and Berry[8] came to the conclusion the accommodation coefficient for gases of high molecular weight was always in the neighbourhood of unity. Langmuir's theory of adsorption indicates that all, or nearly all, the molecules hitting a solid condense and reëvaporate. The accommodation coefficients are therefore virtually unity, and almost all the molecules leave in thermal equilibrium with the filament. This conclusion has been supported by a number of investigations. Recently, however, it has been shown that in certain cases molecular or atomic beams may be reflected specularly from solid surfaces without any transfer of energy.[9]

It therefore seems plausible to assume that energy transfer between complex gas molecules and solids may be highly specific, and that in certain cases the accommodation coefficients may be quite low. This is especially so in the case of molecules which decompose unimolecularly, since such molecules are notoriously specific in action insofar as the transfer of energy is concerned.

The mechanism of the foregoing reactions may therefore be explained on the following basis. With acetone and ethyl ether the molecules are mostly adsorbed on collision. They evaporate after a very short mean life on the surface, and therefore leave in thermal equilibrium with the surface. The inner side of the gas layer next to the filament is therefore at a temperature which does not differ appreciably from the temperature of the filament. No appreciable error is therefore introduced into the calculation of the heat of activation of the reaction. With propionaldehyde and methyl ether the accommodation coefficients may be assumed to be low. (This assumption will be discussed later). Hence comparatively few of the molecules are adsorbed and reach thermal equilibrium with the filament. The majority of the molecules are reflected more or less specularly and very little energy is transferred to them. There is therefore a very abrupt drop in temperature at the surface of the wire, followed by the usual more gradual skin effect. If this assumption is correct, the mean temperature of the layer in which reaction occurs will be considerably below the temperature of the filament itself.

The high temperature coefficient of the reaction may therefore be explained in two ways: (a) We may interpret the high temperature coefficient as being due solely to the cause mentioned above. The temperature scale used in

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[8] Proc. Roy. Soc., 84 A, 576 (1911).

[9] Bradley: Chem. Rev., 9, 47 (1931).

calculating the heat of activation of the reaction should therefore be shifted to somewhat lower temperatures. The heat of activation of the reaction is inversely proportional to $(1/T_1 - 1/T_2)$. If we lower both temperatures by a constant amount, the calculated value of the heat of activation will therefore decrease. To explain the difference in the heats of activation on this ground alone would require a very large temperature drop at the surface of the filament (for propionaldehyde 275°C). It seems much more likely that the following explanation is the true one. (b) It has been observed that accommodation coefficients increase with increasing temperature. We may therefore explain the high temperature coefficient of the reaction in a much more reasonable way by assuming that the accommodation coefficients are low, but not excessively low, and vary with temperature. The temperature coefficient of the reaction is therefore a composite one, and includes the temperature coefficient of the accommodation coefficient. It is thus unnecessary to assume such a pronounced drop in temperature at the surface of the filament.

The specific action of the surface remains to be explained. If the foregoing assumptions are valid, the accommodation coefficients for ethyl ether and acetone are near unity while those for propionaldehyde and methyl ether are quite low. Accommodation coefficients usually rise in the presence of a layer of adsorbed gas. It is therefore by no means improbable that the specific action depends on the relative adsorption of the various products formed in the decompositions. It has been noticed that a small amount of carbon is deposited in the decomposition of propionaldehyde and of methyl ether, but not in the other cases. This would seem to be the most likely explanation of the specificity.

A number of the questions raised above might be settled by a determination of the heat loss from filaments in the presence of the various gases. Such experiments are in progress.

Summary

The kinetics of the thermal decomposition of gaseous dimethyl ether in contact with heated platinum filaments have been investigated. The decomposition is unimolecular and occurs in a hot gas layer surrounding the filament. The heat of activation is found to be 67,000 calories as compared with 58,500 for the homogeneous reaction. The high temperature coefficient may be explained on the assumption that the accommodation coefficient is low, and hence thermal equilibrium with the filament is not attained by colliding gas molecules.

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COLLOIDAL BORON

BY ALBERT L. ELDER AND NAOMA D. GREEN

Svedberg[1] reports that colloidal boron has been known nearly as long as amorphous boron. Kuzel[2] was granted patents for the preparation of colloidal boron. Ageno and Barzette[3] have contributed to the study of colloidal boron. A more extended report was given by Gutbier[4] who prepared sols by reduction of B_2O_3 with Mg, Na, and K. The fusion mixture was purified by treatment with dilute and conc. HCl followed by washing with distilled water until the material which went through the filter was in a colloidal state. His failure to obtain consistent results suggested the possibility of continuing this investigation. Sols prepared using identical procedure by Astfalk and Boss under his direction varied greatly in rate of settling, stability under dialysis, color, rate of flocculation with electrolytes. They recognize that the colloidal boron was not pure boron.

Our preliminary experiments using the procedure outlined by Gutbier gave negative results or at best extremely dilute sols. The general procedure was the fusion of Mg and B_2O_3 in approximately the ratio of 1 to 3. The fused mixture was cooled, pulverized, treated with conc. HCl, and washed on a suction filter with hot distilled water. An extremely dilute sol was sometimes obtained on long washing. Further washing yielded no sol.

In an attempt to prepare a more concentrated sol fusions containing Mg and B_2O_3 in ratios varying from 1 to 10 to 10 to 1 were made. The most concentrated sol was with a mixture of Mg and B_2O_3 in the ratio 1 to 3. It was discovered that refluxing from 0.5 to 1 g of dried purified boron with 100 to 250 cc of distilled water for from 2 to 2.5 hours gave on filtration much more concentrated sols.

The fusion container was an open iron vessel 8.5 cm deep by 4 cm in diameter having walls 4 mm thick. The reaction was started by the use of two oxygen-gas blast lamps which were focused on the lower part of the container. To insure rapid fusion the time of heating was less than five minutes. The reaction once started is very vigorous. It is advisable to grind the fused, cooled mass before treating with conc. HCl.

The addition to the fusion mixture of certain impurities which might have been found in the raw materials of previous investigators altered the concentration of the colloidal material. For example the addition of Na_2SO_4 in concentration of 0.01 and 0.001% of B_2O_3 by weight caused definite increase in the concentration of sols obtained. $NaNO_3$ and NaCl in equivalent concentrations were not as effective as Na_2SO_4. The addition of traces of iron filings to the fusion mixture increased the concentration of the sol.

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[1] Gutbier: Kolloid-Z., 13, 137 (1914).

[2] British Pat., 25,864; French Pat., 371,799; German Pat., 197,379; C. A., 1, 1930 (1906).

[3] Atti. Accad. Lincei, 1, 1824 (1910).

[4] Kolloid-Z., 13, 137 (1914).

Study was made of some of the properties of these sols. The sols prepared by refluxing were found by electrophoresis measurements to be electronegative. The acid sols were coagulated very quickly when subjected to 220 volt potential while the neutral sols were not. Since the colloidal boron was prepared by refluxing the fusion residue with boiling water the sols are obviously rather insensitive to coagulation by heat.

In contrast with the colloidal solutions of boron reported by Gutbier[1] and others[2] the sols prepared in these experiments were extremely resistant to coagulation by electrolytes. HCl, 1 N $Al_2(SO_4)_3$, 1 N $CaCl_2$ and 1 N NaCl gave no decisive coagulation in any concentrations. The addition of crystals of $Al_2(SO_4)_3$ and of $SnCl_4$ was effective only in exceedingly high concentrations.

Mixing boron and iron sols caused complete coagulation of both. The concentration of iron in the iron sol used was 4.27×10^{-4} g/cc. One cc of the iron sol coagulated 3 cc of boron sol in one hour. The concentration of solid matter in the boron sol was 0.052% of the total weight. On ultrafiltration of this sol, and evaporation of the ultrafiltrate a residue of 0.017% was obtained. This indicates that it was the electrolyte present in the boron sol which coagulated the iron sol which in turn carried down with it the colloidal boron. The boron sol ultrafiltrate was effective in equivalent concentration in coagulating the $Fe(OH)_3$ sol.

All attempts at concentration of the boron sol by pervaporation and dialysis were unsuccessful. Attempts to stabilize the sol by addition of gelatin solution to give total gelatin concentrations of 0.02% to 0.4%, as well as soap solution to a concentration of 0.4% and of a trace of zinc ammonium alginate were unsuccessful. The addition of a trace of glycol bori-borate had some effect in slowing the rate of sedimentation.

The rate of settling in refluxed sols was much slower than that in sols prepared by direct washing. Most of the sedimentation in the first case took place in from one week to two or three months and in the second case always within four days.

A brief study of the preparation of boron sols by the reduction of B_2O_3 with Na showed the sols to be similar to those described above but blue or bluish green in contrast with the yellowish brown sols obtained from the Mg reduction. The stability of these sols was increased from several hours to three months by refluxing although the concentration was not greatly increased.

The following results are indicative of the adsorptive capacity of the boron used. Percent adsorption by weight, ethyl acetate 17.5, acetone 20.8, benzene 14.3, ethyl alcohol 8.7, water 7.6.

Summary

A method for the preparation of and some of the properties of colloidal boron are described.

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[1] Kolloid-Z., 13, 137 (1914).

[2] Ageno and Barzetti: Atti. Accad. Lincei, (5) 1, 1824 (1910).

A NEW THEORY OF EMULSIONS

BY C. H. M. ROBERTS

An emulsion, as is well known, consists of a stable dispersion of one liquid in another liquid. The factors which appear indispensable for the formation of an emulsion are, first, that the two liquids be mutually immiscible; second, that there be suitable agitation to cause the dispersion of one liquid in the other; and third, that there be present in one liquid—or in both—some substance or substances which have the property of protecting the liquid-liquid interface, so as to prevent contact and coalescence of the droplets of the dispersed phase. In general, it is considered that this material, which is called the emulsifying agent, is present in the continuous phase of the emulsion. The approximate truth of these generalisations has been amply demonstrated and may be accepted without question. The problem of emulsions, then, resolves itself chiefly into the determination of the physical characteristics, chemical composition, and mode of operation of the emulsifying agent.

As to the physical characteristics of the emulsifying agent, it has been rather generally considered that the material is colloidally dispersed in the continuous phase of the system, altho this is by no means a hard and fast rule, since it has been demonstrated that emulsions can be stabilized, on the one hand, by molecularly dispersed materials and, on the other hand, by finely ground solids, whose sizes are much greater than the upper limits usually given for colloidal dispersions.[1] As to the composition of materials suitable for stabilizing emulsions, practically any material may be employed, with suitable combinations of the two primary liquids, the only requirement being that it shall be soluble, dispersible or wettable in or by one of the liquids. As to the mode of operation of the emulsifying agent, it is generally considered that it functions by being adsorbed at the liquid-liquid interface, on the side exposed to the continuous phase, and thereby prevents contact and coalescence of the droplets of the dispersed phase.

Numerous theories have been advanced, from time to time, to explain the observed facts as to the formation and stabilization of emulsions, but these theories are too well known to require extensive consideration at this time.[2] The *phase-volume* theory of Ostwald presumed that the type of emulsion—that is, oil-in-water or water-in-oil—was related to the percentages of the two phases present. This theory is no longer considered valid. The *viscosity theory* of emulsions has been tested and found wanting and it is now believed that viscosity is a factor which affects emulsions principally by hindering

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[1] Holmes: J. Phys. Chem., 29, 1205 (1925).

[2] Clayton: "Theory of Emulsions," Chap. 3, (1928).

coalescence of the dispersed droplets.[3] In this connection, Wilson and Ries[4] have shown that interfacial films may have viscosity characteristics which enable them to be considered as plastic solids. The question of viscosity therefore must be considered in relation to the interfacial zone, as well as to the liquid phases. The *hydration theory* of Fischer presumes that the emulsifying agent forms, with the continuous phase, a hydration compound, in which the other phase is dispersed. This theory is inadequate to explain some of the observed facts and is in conflict with other observed facts. It cannot, therefore, be considered an adequate theory of emulsions. The *surface tension theory*, or more properly the *interfacial tension theory*, has been extensively investigated and has been found adequate to explain the formation and stability of many emulsions. This theory has merged into the more modern and more widely accepted *adsorption-film theory*, which explains the formation and stability of emulsions on the basis of the formation and stability of an adsorbed film at the interface. A modification of the adsorption-film theory was presented before the First Colloid Symposium, by Finkle, Draper and Hildebrand.[5] Their theory was based upon the work of Harkins and Langmuir, who proved the oriented adsorption of polar molecules at interfaces and who advanced the idea that there is a relation between the shape of the adsorbed molecules and the degree and direction of curvature of the interface. The factors of angle of contact and electrical characteristics of the adsorbed materials also enter into various theories.

From this very brief and inadequate summary of former theories of emulsions, we will now proceed to a consideration of the new theory to be presented. This theory has been developed, in connection with an exhaustive study of petroleum emulsions, because existing theories have been found inadequate to explain many of the relations found, and is the result of more than eight years' intensive investigation of such emulsions, both in the laboratory and in the field. While petroleum emulsions are predominantly of the water-in-oil type, there are, however, natural petroleum emulsions of the reverse type. Consequently, the theory has had to consider both types and has had to be developed in spite of the very meager information as to the chemical composition and physical properties of the materials entering into such emulsions.

Considering oils as a broad class of materials, it may be said that they consist of a complex mixture of liquid molecules of low polar moment, in which are dissolved or dispersed greater or less amounts of materials of higher polar moments and that some or all of these materials undergo a greater or less degree of ionization. Such a definition can, it is believed, be considered to broadly cover any non-aqueous solution. Previous experience and general

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[3] It must be appreciated, of course, that the effect of viscosity is more far-reaching than is here indicated. Viscosity enters into the mechanism of emulsion-formation, by decreasing the speed of adsorption; as well as into the mechanism of emulsion-resolution, by decreasing the mobility of the droplets of the dispersed phase, as well as hindering their close approach and coalescence.

[4] Colloid Symposium Monograph, 1, 145 (1923).

[5] Colloid Symposium Monograph, 1, 196 (1923).

knowledge indicate that it is the relatively highly polar and ionized constituents of these oils which are of most importance in determining the emulsification characteristics of an oil.

Considering the brines, associated with crude oils, as a broad class and having in mind the high ionizing power of water as a solvent, it may be said that they are complex mixtures of dissolved salts, which are, in general, highly ionized. There may also be present, in this aqueous solution, more or less dissolved or dispersed organic material, which will be relatively highly polar and may be more or less ionized. Such a definition can, it is believed, be considered to cover broadly any aqueous solution. The emulsification characteristics of the aqueous phase will, therefore, depend upon the kinds and concentrations of ions and polar molecules present.

With reference to the effects of ions, Michaelis[6] makes the very simple assumption that hydroxyl ions are more capillary active than hydrogen ions. Since both these ions have the same magnitude of charge (altho of different sign), while their masses differ greatly, it seems reasonable to extend Michaelis' assumption and to say that the adsorbability of ions at free surfaces increases as their charge to mass ratio decreases. It is, of course, understood that the ions are, probably in all cases, more or less hydrated, which serves to increase their effective mass and may decrease their effective charge. This assumption serves to explain the observed facts that a free distilled-water surface displays a negative charge and that the magnitude and sign of charge of the free surface of aqueous solutions depends upon the concentration and kinds of ions present in solution. The observed great effect of hydrogen and hydroxyl ions on the surface charge, as discussed by Michaelis,[6] also serves to indicate the importance of pH of the aqueous phase of emulsions.

Especially in connection with adsorption at free liquid surfaces, it is impossible to ascribe attractive forces to a mathematical surface. Therefore the explanation of Michaelis,[6] that such adsorption is "apparent" and arises from the forces acting within the liquid, is believed to be entirely acceptable. Another way of looking at the question is that such adsorption is due to "rejection" of the adsorbed material from the body of the liquid, the material "rejected" being that which has the lowest charge to mass ratio. Incidentally, the concentration of such material at the surface will accomplish the maximum reduction of surface energy, which is a basic principle of physical chemistry. Adsorption at free liquid surfaces may, therefore, be ascribed to an "exclusion effect," whereby the material is pushed to the surface because it is attracted back into the mass of the system with less force than acts on the other constituents of the system.

The conclusion of the preceding paragraph, as will be immediately apparent, is exactly parallel to the "attraction intensity" principle of Traube.[7] From Traube's principle, we see that adsorption increases with decreased attraction intensity toward the body of the solution and with increased attrac-

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[6] Alexander's "Colloid Chemistry," 1, 497 (1926); see, also, "Hydrogen Ion Concentration," Chap. X (1926).

[7] Alexander's "Colloid Chemistry," 1, 640 (1926).

tion intensity toward the adsorbent. This principle is adhered to in developing the characteristics of adsorption at interfaces.

The above discussion has been more or less restricted to ion adsorption, while it is also necessary to consider molecule adsorption. Molecules of all substances have greater or less external electromagnetic fields, which arise from the presence and motion of positive and negative charges in the atoms composing the molecules. According to the dissymmetry of distribution and the characteristics of motion of these charges within the molecule, it will be more or less polar, that is, it will have definite electric and magnetic moments. This has previously been discussed by Harkins.[8] While a molecule contains exactly equivalent amounts of positive and negative charges and is, therefore, exactly neutral, the unsymmetrical distribution of those charges gives the same external effect as though the molecule was positively charged at one end and negatively charged at the other. It may therefore be considered analogous to a pair of ions very close together and constrained to move as a unit but, with reference to either end, as having a small charge. We may, therefore, as for ions, speak of the charge to mass ratio of molecules and it is evident that, even for highly polar molecules, the ratio is extremely small, as compared to that of ions of even very large mass. In addition, the strong portion of the external field of a polar molecule extends over a very small space (comparable to molecular dimensions) and outside of this space the molecule acts as though it were practically neutral; whereas this is not at all true for ions.[9]

From the above considerations, it follows that polar molecules will adsorb at a free surface in preference to ions, since the surface energy is thereby decreased to a greater extent. Due to the vector character of the fields of polar molecules, it also follows that they will orient in a free surface so as to expose their least polar portions. It may be noted that the fields of ions are vectorial and that adsorbed ions will also be oriented. Since both polar molecules and ions will be present in the same solution, it follows that both the polar molecules and those ions having the lowest charge to mass ratio will tend to accumulate in the surface. That is, there will be competition between ions and molecules for positions in the surface. Since the mobility of ions is much greater than that of molecules, it also seems probable that, when a free surface is suddenly formed, the 'adsorbable' ions will reach that surface considerably in advance of the molecules but will be slowly displaced by polar molecules as the age of the surface increases. That is, in the early stages of adsorption, we may consider the process to be (chiefly) ion adsorption, which is dynamic and reversible and which proceeds toward or to equilibrium; followed by molecular

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[8] Alexander's "Colloid Chemistry," 1, 199 (1926).

[9] The concept of polar molecules as magnetic dipoles, as well as electric dipoles, while not made use of at this time, is now being investigated. It is mentioned here to call attention to its possible application and will be incorporated into the theory when and if adequate data are obtained. It is obvious that a complete description of the properties of ions and molecules will have to include both their magnetic and electric properties but that this will introduce only such changes into the theory as may be consequences of the relative moments of the two forces. The success of present theories based on electric forces alone indicates that only in relatively few cases will introduction of the magnetic moments necessitate appreciable revisions of theories.

adsorption, which proceeds to equilibrium. In the final state, then, the surface will consist of an equilibrium mixture of "adsorbable" ions and polar molecules, in which the proportion of ions to molecules present will depend upon their relative mobilities, concentrations and the tenacity with which they persist in the surface. In the final state, especially where molecular adsorption is high, it is entirely possible that the surface layer may approach static conditions and become more or less completely irreversible.

The concept of the Helmholtz double layer is adhered to in the present theory. However, the double layer, as is apparent from the preceding discussion, is considered to contain both ions and polar molecules. From the preceding discussion, it is also apparent that the oriented adsorption of polar molecules does not differ at all from the adsorption of layers of ions of opposite polarity, except that in the former case there is a 'rigid' binding between the positive and negative charges at opposite ends of polar molecules, whereas such is not the case where positive and negative ions are concerned. Mooney presented, at the Eighth Colloid Symposium,[10] the concept of the mutual adsorption of ions and molecules, while McBain and Williams, at the Seventh Colloid Symposium,[11] presented certain numerical results as to the ratio of ions to molecules adsorbed at free surfaces.

In determination of interfacial potentials, by cataphoretic or streaming potential technique, the new theory proposes that the shear zone, across which the potential difference is measured, is located between the primary, mono-molecular surface layer and the underlying 'diffuse' atmosphere of ions and molecules. This view is taken primarily because of the results of Harkins and others, who have shown that surface layers are usually, if not always, mono-molecular; whereas Fahrenwald[12] and others have shown that surface layers may be poly-molecular. This apparently conflicting evidence may be made concordant by merely assuming that the method of one investigator showed the concentration of material in the primary layer; while that of another showed the total concentration of material in the 'adsorption zone' at the surface. The reason for assuming that the zone of shear does come between the primary, mono-molecular layer and the inner diffuse zone is that, at that place there is the greatest discontinuity of properties between the opposite sides of adjacent layers.[13] Since it is considered that ions and molecules are mutually adsorbed in a surface, the primary layer is considered to consist of both these components, in proportions dependent upon the previously discussed factors.

To complete this picture of surface adsorption, it may be noted that, in the case of a solution in which negative ions are preferentially adsorbed, while the preferred orientation of polar molecules is with the negative ends exposed, the surface charge will vary, with the age of the surface, from zero to a maximum negative value, corresponding to the (approximate) equilibrium

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[10] J. Phys. Chem., 35, 331 (1931).

[11] Colloid Symposium Monograph, 7, 105 (1930).

[12] Trans. Mining Met. Engrs., 70, 724 (1924).

[13] Andrews: Colloid Symposium Monograph, 7, 119 (1930).

of ion adsorption; thru zero, corresponding to an electrical equivalence between adsorbed ions and adsorbed molecules; to a low positive value, corresponding to an equilibrium of molecular adsorption, in which there is an electrical preponderance of molecules over ions in the surface. It will be seen that this concept permits the explanation of surface charges varying, with time, in both magnitude and sign, without the necessity of postulating different mechanisms of action.

Although it has not been specifically mentioned before, it is to be understood that, in speaking of ions and molecules, those terms refer to ions and molecules in the state of solvation or hydration in which they exist at the place and in the system considered. Each ion and molecule in solution is considered to be the nucleus of an adsorption complex so arranged as to minimize the abruptness of transition of properties between the components of the solution, the effect being entirely analogous to adsorption at interfaces. It is these complexes which adsorb at surfaces or interfaces. Adsorption of these complexes, however, may and probably will result in changes in the solvation conditions and this may be expected to materially alter the characteristics of the boundary layer. There must also be considered the additional probability that physical interaction across the interface will result in further alteration and distortion of these complexes.

The preceding discussion has been directed to a consideration of conditions at a free surface, whereas, in dealing with emulsions, it is necessary to consider conditions at liquid-liquid interfaces. These conditions will now be discussed.

It is known that, usually, in the case of natural brines and oils, the surface energy of the aqueous phase exceeds that of the non-aqueous phase. It therefore follows that the most stable emulsion condition is that in which the aqueous phase forms the dispersed phase of the emulsion. In cases where the reverse condition is true, the aqueous phase forms the continuous phase of the emulsion. There seems to be no reason why this cannot be accepted as generally true for all emulsion systems. From this it follows that the conditions at a water-oil interface, where water is the dispersed phase, are similar to the conditions at a free water surface. That is, the energy level on the water side of the interface is greater than that on the other side. Therefore the character of adsorption on the water side of an interface will be much the same as at a free water surface, except that more-polar materials will concentrate at the interface than at a free surface, since the energy on the other side of the interface is now materially greater than zero, whereas it approaches zero on the air side of a surface. The conditions on the oil side of the interface will, however, be quite different from those at a free surface of the same oil. The energy level on the water side of the interface will now be greater than that on the oil side, instead of (practically) zero, as it is on the air side of a surface. Therefore the adsorption conditions on the oil side of a water-oil interface will be different both in magnitude and kind from those at a free oil surface. Instead of the least polar materials being in the primary layer, the most polar materials will concentrate there. The conditions may be made somewhat more evident by referring to Fig. 1 in which adsorption at liquid-air and liquid-liquid interfaces is diagrammatically represented.

Another way of arriving at the same conclusions is by the application of the principle stated by Harkins, that adsorption will proceed at an interface in such a manner as to decrease the abruptness of transition of properties from one phase to the other. In the case considered, the energy level in the oil is low, while that in the water is high. Therefore adsorption on the water side will be such as to place the less-polar materials in the water side of the interface, while adsorption on the oil side will be such as to place the more-polar materials in the oil side of the interface. It is entirely possible that the difference in character of adsorption at free surfaces and at interfaces may be the cause of the failure of Antonow's law for interfacial tension as a function of the surface tensions of the separate, mutually saturated, phases.

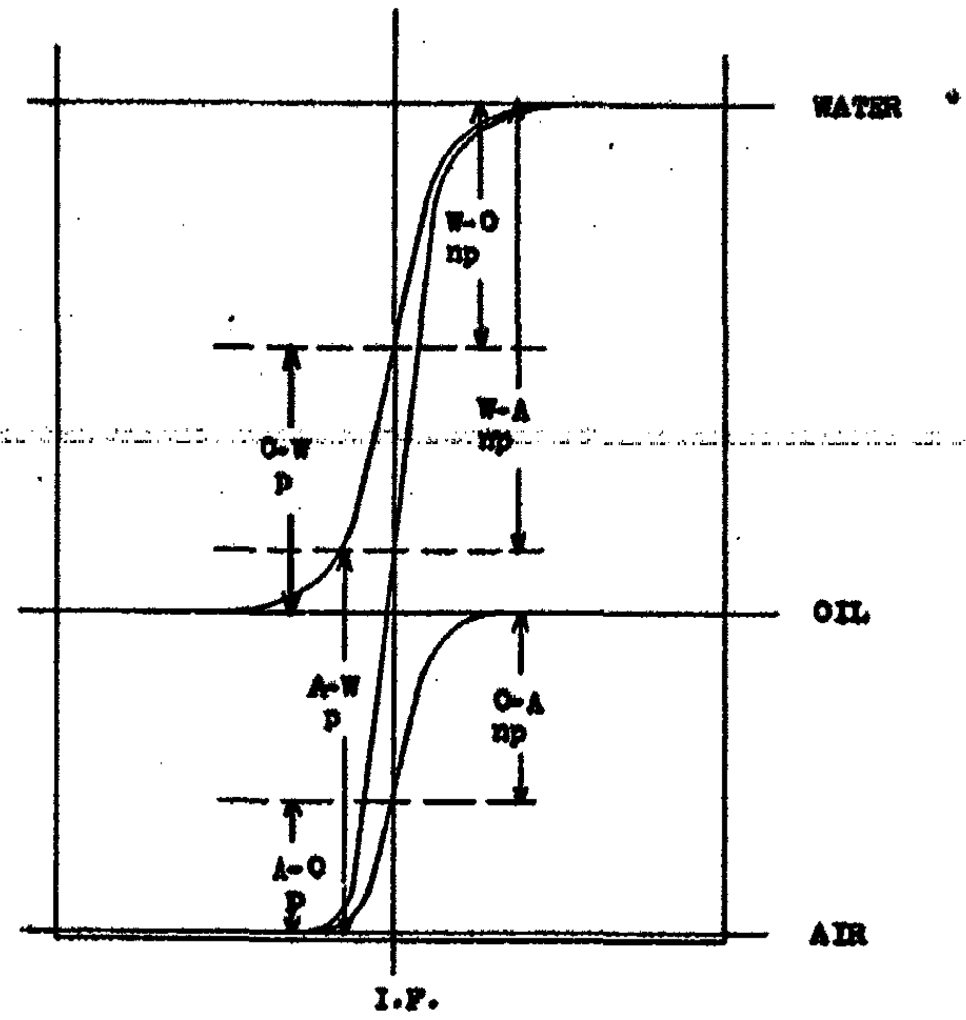

FIG. 1

Diagrammatic Representation of Adsorption at Liquid-Gas and at Liquid-Liquid Interfaces. Horizontal axis represents distance from interface. Vertical axis represents character and intensity of adsorption. Letters in the figure indicate the side of the interface considered, *i.e.*, O-W means the oil side of an oil-water interface, while W-O means the water side of the same interface. The lower case letters are 'p' for polar adsorption and 'np' for non-polar adsorption.

As will be apparent from the foregoing discussion, this theory involves the consideration of adsorption on both sides of an interface. It therefore follows that an interfacial layer must be at least a double mono-molecular layer, providing no interaction occurs between the opposing elements. If such interaction does occur, as for example between hydrogen ions in the primary layer on the water side and fatty acid ions in the primary layer on the oil side, then a molecule of fatty acid may result, the hydrocarbon end of which is in the oil and the carboxyl end in the water. Such an effect, as is obvious, is quite analogous to the postulated mechanism of contact catalysis. Of course, the same sort of thing may occur, as shown by Harkins, in the case of a molecule in either phase, but partially soluble in the other, without postulating the interaction of ions. Such a condition should give rise to an extremely stable interface and this is known to be the case. If the hydrocarbon end is shorter, making the molecular more polar and more water-soluble, its efficiency as an emulsifying agent should be lower, as is the case. If the hydrocarbon end is much longer, making the molecule less polar and more oil-soluble, its efficiency as an emulsifying agent again decreases. It therefore follows that those fatty acids and their derivatives, whose ratio of polar moment to molecular weight lies between certain limits, should be the most efficient emulsifying agents of their class and this is known to be the case.

At the risk of digressing somewhat from the principal topic of petroleum emulsions, it seems desirable to discuss some phases of the emulsion problem which appear to have offered much difficulty of explanation under prior theories.

There is the problem of antagonistic emulsifiers, of which the case of sodium and calcium oleates has been chosen as an example. We know that sodium oleate stabilizes oil-in-water emulsions, that calcium oleate stabilizes the reverse type, while suitable proportions of the two substances result in no emulsion. The latter condition is the one which requires elucidation. In terms of this theory, calcium oleate in the oil will tend to adsorb on the oil side and will try to pass its polar end into the water, while sodium oleate in the water will tend to adsorb on the water side and will try to pass its non-polar end into the oil. This competition for positions across the interface will actually result in mutual repulsive reactions between the competing molecules, so that neither achieves its purpose, if they happen to be present in a certain proportion, and no emulsion forms. If the proportions differ from the critical, the external phase of the resulting emulsion is the one which contains the excess of soap. It may be noted that repulsive reactions across the interface, between adsorbable ions of like charge, would operate to reduce stability, in a manner similar to that just discussed.

A difficulty of the theory proposed by Finkle, Draper and Hildebrand,[5] which caused considerable discussion, was the case of an emulsion of benzene in water, with stearic acid in the benzene as the emulsifying agent. This emulsion apparently contradicts the principle that the emulsifying agent should be in the continuous phase. The explanation of the observed facts, under the new theory, is that, although stearic acid is soluble in benzene and is alleged to be insoluble in water, nevertheless, since benzene is extremely non-polar, while the carboxyl end of the acid is highly polar, adsorbed acid molecules project so far into the water phase that it is no stretch of the imagination to consider that they are actually in the water phase, with only their (extreme) ends projecting into the oil. In other words, the acid is "interfacially" soluble in water, although it may not be appreciably "volumetrically" soluble. This case will now fall nicely into line with Bancroft's principle.

Such an effect as is here postulated may serve at least as a partial explanation of the reversal of some emulsions by agitation. If the solubility is a function of the ratio of exposed surface to total mass, as has been proved in other connections, then it is not hard to see that, since agitation decreases particle size in emulsions and therefore increases this ratio, it may well change the "interfacial" solubility of some materials sufficiently to cause a reversal of emulsion type. In this case, then, the change in emulsion type is really due to an effective change of phase of the dissolved material, even though it is "insoluble" in one phase. Something along the same line is discussed by Taggart,[14] in connection with the degree of solubility of flotation agents. Bartell and Mack[15] also refer to the same sort of thing. They say, "Surface films are of two types, namely; those formed by insoluble highly adsorbed substances and those formed by soluble and less strongly adsorbed substances." The application of the quotation to this portion of the discussion is that the substance, which is presumed to cross the interface into the phase in which it is "insoluble," will be very strongly adsorbed; while that portion of it in the phase in which it is soluble will not be strongly adsorbed. Hence the effective "emulsifying agent" is in the external phase, in accordance with Bancroft's principle.

The question of dual phase emulsions has been extensively investigated, especially by Seifriz,[16] although his results were obtained by the addition of materials to the system, to cause reversal of type. The residues of dispersed oil, within globules of water themselves dispersed in the bulk of the oil, no doubt owe their stability to differences in the emulsifying agent, as Seifriz observes. The present viewpoint relative to dual emulsions, which are sometimes encountered in petroleum systems, considers the case under conditions when there has been no addition of chemicals to the system and when the production conditions are such as to make it fairly certain that the oil and water enter from a single horizon and hence are uniform in composition. The suggested explanation follows from the previous discussion relative to interfacial solubility and the effect on that solubility of alteration of area/mass ratio.

It is known that, when oil and water are agitated together there is a tremendous range of particle sizes produced and there is also considerable dual dispersion. If we assume the case of an emulsifying agent having the "interfacial solubility" postulated, we can easily see that the solubility relations may be sufficiently different on droplets of different sizes, so that the "emulsifying agent" exchanges phases at the interfaces of the smallest droplets and we are left with stable droplets of oil dispersed in water, which is itself dispersed in more of the "same" oil. In connection with natural dual emulsions, it may be

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[14] J. Phys. Chem., 36, 152 (1932).

[15] J. Phys. Chem., 36, 65 (1932).

[16] J. Phys. Chem., 29, 738 (1925).

remarked that they are relatively rare, which checks with the low probability of simultaneous occurrence of the necessary combination of properties of oil, water and "emulsifying agent."

To return to the principal topic of discussion, it was previously stated that the problem of emulsions consists chiefly of the determination of the physical characteristics, chemical composition and mode of action of the emulsifying agent, which has usually been considered to be a material present in the external phase of the system. From the preceding discussion, it seems apparent that the emulsifying agent can no longer be considered as a single material in one phase of the system, since the interfacial zone may consist of two Helmholtz "double layers," one in each phase, or it may consist of a "compound" Helmholtz double layer, whose central portion consists of molecules "straddling" the interface. These "straddling" molecules may be formed by interfacial reaction of ions from the two phases or by the "sharing" between phases of molecules partially soluble in both. The problem has therefore become complicated to the extent that the composition of both phases of the system must be subjected to examination, since any component of either phase of the system may, under suitable conditions, aid in stabilizing the interface.

In the study of naturally occurring emulsions in the petroleum industry, the problem is still further complicated by the fact that practically nothing is known about the composition of the various components of the oil phase or what components of that phase contribute to emulsion stability. Considerably more is known about the composition of the aqueous phase of such systems but even that is incomplete and inadequate, since natural brines are usually analysed only for their content of common inorganic constitutents. However, it is felt that the situation is by no means hopeless or even very discouraging. There seems no reason to worry excessively over the lack of information as to composition, because it is believed that, whatever the composition, it is the physical properties which determine the emulsification characteristics of the system. Therefore, if those properties, and especially those of the interfacial layer, can be determined, it is believed that sufficient information will have been obtained to enable the essential properties of the emulsion, under changed conditions, to be predicted.

In the light of the foregoing remarks, it is now desired to draw a picture of the mechanism of formation of an emulsion interface, according to the new theory. The formation of a water-in-oil emulsion will be described.

At the instant of formation of an interface, the opposed surfaces of the respective phases will have the same average concentrations of components as any cross-section within the respective volumes; that is, no adsorption has yet taken place. At this instant, also, the electrokinetic potentials on both sides of the interface, by definition, are zero and the interfacial tensions on both sides will have their maximum dynamic values. Ions and molecules immediately begin to move toward the interface, but the ions arrive first because of their higher mobilities. Ions of high polarity tend to accumulate in the interface on the oil side; while ions of low polarity tend to accumulate in the interface on the water side.

Neglecting molecular adsorption for the moment, we can consider that equilibrium of ionic adsorption is attained, at which instant the electrokinetic potentials will have attained maximum values. While this equilibrium is being reached, the interfacial tensions will fall with extreme rapidity, while the electrokinetic potentials will increase with corresponding rapidity.

From this stage of the process we must consider the relatively slow moving molecules, which are beginning to concentrate in the interface and crowd out the more mobile ions. To simplify the picture, we will consider that the aqueous phase consists only of a solution of simple inorganic salts and that no "interfacial compounds" are formed. This enables us to dismiss the water side of the interface from further consideration and leaves that side at the ionic equilibrium stage, with the least polar ions present in the primary layer. On the oil side, the replacement of ions by polar molecules, oriented with their most polar ends toward the water, will proceed continuously. When the point is reached where there is electrical equivalence between the ions and polar molecules on the oil side, the corresponding electrokinetic potential will be zero, while the rate of change of interfacial tension on the oil side will have reached a low value.

As the age of the interface continues to increase beyond this point, there will be an increasing preponderance of molecules over ions in the interface, until the static condition, of a complete mono-molecular layer of polar molecules in the primary layer, is reached. At this time, the electrokinetic potential on the oil side will have attained a low steady value, of opposite sign to that in the early stages of the process, and the interfacial tension will have attained its minimum static value.

It will be noted that attention is repeatedly drawn to the existence of electrokinetic potentials and interfacial tensions on both sides of the interface. This is believed to be entirely valid, even though the primary layer consists of molecules "straddling" the interface, because there are markedly different conditions existing between the primary layer on the oil side and the adjacent oil phase, from those existing between the portions of the corresponding region on the water side. Distinction is made today between electrokinetic potentials in the two phases, although these are commonly measured only for the external phase. From the same point of view, it is entirely probable that, as Bancroft pointed out many years ago, there are two interfacial tensions, one on each side of the interface. These complications in the study of emulsions are unfortunate, but they seem to be inescapable conclusions of the present theory.

Whether or not the conditions of zero potential or reversal of potential, on the oil side, occur as described, obviously depends upon the relative concentrations, polarities, etc., of the adsorbable materials in the oil phase. It may also be pointed out that, if the primary layers on the two sides consist of ions which react to form molecules "straddling" the interface, the progression from ionic to molecular adsorption will occur synchronously with ionic adsorption, despite the fact that there may be no adsorbable polar molecules in the system. It has been pointed out by Clayton,[17] who referred to work of Powis,[18] that electro-

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[17] "Theory of Emulsions," 21 (1928).

[18] J. Chem. Soc., 109, 734 (1916).

kinetic potentials at the surface of oil drops dispersed in water decrease with increasing time. The explanation of the effect was not given. In addition, work on certain naturally occurring emulsions, performed in our laboratory, has clearly demonstrated the reversal of potential on the external, oil side of the interface. The emulsions when fresh showed strong negative cataphoresis, which gradually became weaker, then ceased entirely and later changed to weak positive cataphoresis, the whole process requiring about two months for completion. As far as is known, this reversal of interfacial potential in emulsions has not heretofore been observed, would not have been expected under prior theories and could not have been easily explained. The present theory offers a simple explanation of this phenomenon and of that observed by Powis and the observations on reversal of potential were taken as a result of the prediction of the theory that such an effort might occur in certain emulsions. The observations are therefore considered to afford striking confirmation of the essential validity of the theory.

As to the proposition of different interfacial tensions on the two sides of the interface, the situation is more difficult. While it seems entirely probable that this is the case, the measurement of these tensions is more difficult and has not yet been attempted. It is possible that a modification of the sessile drop method could be employed, but it has not seemed profitable for us to attempt it. However, another method of measurement has been used, which, although its true significance has not yet been discovered, has nevertheless yielded results which have shown a surprisingly close correlation with some of the properties of emulsions.

This method involves the measurement of interfacial tension by the ring method and makes use of the excellent correction factors experimentally developed by Harkins.[19] DuNouy[20] notes that there is often a difference in the values of interfacial tension, according to whether the ring is pulled from water to oil or pushed from oil to water. The statement is made that the values from oil to water are "too low," but that the values from water to oil "check perfectly even when the ring has passed through the oil before reaching the water." Natural curiosity as to these statements, together with the idea of the existence of different tensions on the two sides of the interface, led to a series of measurements with known liquids. The results were most surprising, in that they showed a high degree of regularity in the sets of measurements, an often large difference between corresponding measurements of "push" and "pull," and an apparently close relation between the measurements in a given direction and the kinds of materials dissolved in the phase into which the ring passed.

The forms of the curves and the values obtained are illustrated in Fig. 2, which shows the results of a series of measurements made with a certain sample of Nujol against distilled water and solutions of sodium chloride, hydrochloric acid and sodium hydroxide. Portions of a single sample of water were used in all cases and the chemicals were the purest obtainable but were

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[19] J. Am. Chem. Soc., 52, 1751 (1930).

[20] "Surface Equilibria of Colloids," 173 (1926).

not specially repurified. In each case, the amount used was 5 grams of material, on an anhydrous basis, dissolved in 100 grams of water. The chemicals used were Baker's C. P. Analysed. The water was specially distilled and tested for purity by constancy of surface tension.

As will be seen in the figure, in the case of distilled water, the push and pull values are coincident. In the cases of salt and of acid, the pull values are coincident with the distilled water values, while the push values are materially lower and do not coincide. In the case of caustic soda, the values of both push and pull are materially different from the previous determinations. The coincidence of the pull values in every case but the last makes it appear that this measurement indicates something about the conditions in the oil phase, while the push values indicate something about the water phase. As to the case of caustic soda, the natural conclusion is that the Nujol has changed and this is the case, since we had already determined, in an entirely different connection, that caustic soda is quite soluble in Nujol. The large effect of caustic soda on the interfacial tension, which agrees with Fahrenwald's observations[21] on benzene, but is contrary to Harkins' results[22] with benzene, led to discussion

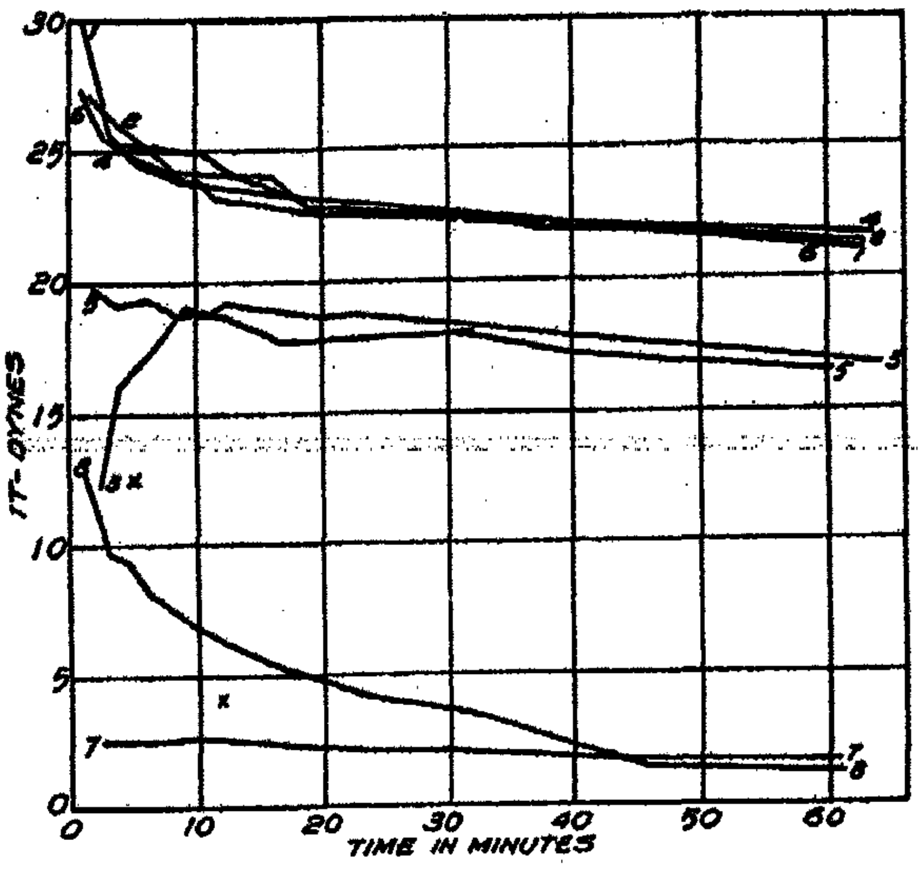

FIG. 2
Interfacial Tensions
NUJOL vs AQUEOUS SOLUTIONS
Odd numbered curves—IT measured by pushing from Oil to Water
Even numbered curves—IT measured by pulling from Water to Oil
Curves 1 and 2—Nujol vs Distilled water Temp. 85°F
" 3 and 4— " " " " plus 5% NaCl " 70°F
" 5 and 6— " " " " " " HCl " 72°F
" 7 and 8— " " " " " " NaOH " 78°F
Concentration of Solutes—5 g. per 100 g. Water.
Determinations made with DuNouy Interfacial Tensiometer and corrected by use of Harkins' factors (J.A.C.S. 52, 1751).

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[21] Trans. Mining Met. Engrs., 70, 682 (1924).

[22] J. Am. Chem. Soc., 39, 549 (1917).

of the subject with Dr. Harkins, who suggested the desirability of a check by the drop method. The results of this check are shown by the crosses in the figure, the higher value being for drops whose formation time was five minutes, while the lower was for twelve minute drops; the measurements being for water dropped into oil. While it is recognized that these short times of drop formation probably involve dynamic effects and lack of interfacial equilibrium, the tests nevertheless served the desired purpose of substantiating the results yielded by the ring method and proved that, in this system at least, caustic soda has a large lowering effect. Another test, which attempted to eliminate some of the uncertainty, was made by allowing a partial drop to form and then stand quietly. This drop gradually lengthened and, 3½ minutes after the stop cock had been closed, detached from the dropping tip. It therefore seems quite evident that the interfacial tension was actually and considerably lowered by the caustic soda.

From these and hundreds of other similar measurements, both on controlled systems and on natural brine-oil systems, it is apparent that there is no reason for calling a set of "pull" measurements correct and a set of "push" measurements incorrect or low. As a matter of fact, it is not at all uncommon, especially with natural oils and brines, to find ratios of push to pull values which vary from 10/1 to 1/10, or which, in a given system vary, with time, in the same manner. It therefore appears that there is a place for both types of measurement, that they have a real significance and that they are related, in some manner yet to be discovered, to the adsorption conditions on the two sides of the interface. In view of the simplicity of the measurements, they seem to offer a fruitful field for investigation and it is rather astonishing that results such as these have not been published before.

One obvious difficulty with the measurements is, of course, as was pointed out by Dr. Harkins, the question of relative wettability of the platinum ring by the two liquids. It is planned to repeat certain series of these measurements, using pyrex glass rings, which have recently been constructed. Preliminary measurements of surface and interfacial tensions, using both platinum and pyrex rings, can, however, be reported at this time.

Surface tensions of water, benzol and Nujol give values agreeing closer than one percent, from which it may be concluded that contact angles do not enter appreciably into such measurements. This is in agreement with the known reliability of platinum ring measurements of surface tension of the most diverse materials. It also is in agreement with Harkins's views, as expressed in his paper concerning the ring method for surface and interfacial tension.[22]

Interfacial tensions, both push and pull, for the system distilled water-Nujol, have been made, using both types of rings. The values measured from water to oil show excellent agreement, whereas the values measured from oil to water differ by nearly fifty percent. The scope of the measurements is not sufficient to warrant any conclusions at this time, but it is believed that the

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[22] J. Am. Chem. Soc., 52, 1770 (1930).

effects may be referable to differences in surface energy relations platinum-oil and platinum-water, as compared to the relations glass-oil and glass-water. If this is at all correct, it may be expected that interfacial tension measurements, relatively free from angle of contact effects, may be expected from rings whose surface energy is either very low or very high, as compared to those of the materials whose interfacial tensions are to be measured. A series of measurements, with rings of different materials, will be made in the near future, in an effort to discover something definite about these relations. It is also suggested that information as to surface energy characteristics of solids may possibly be deduced from such interfacial tension measurements, in a fixed oil-water system, using rings, discs, knife edges, etc., of various materials.

A consideration of the observed facts of the dependence of interfacial potential on the age of an interface, in a given emulsion system, and of the reversal of sign of potential in some emulsions, leads to the conclusion that the stability of an emulsion interface is not necessarily related to the potential. This is in at least qualitative agreement with the observed lack of relation, in many cases, between the stability of emulsions and the interfacial potential and the fact that some emulsions and colloidal dispersions fail to coagulate at zero or at the so-called critical potential. From the present theory, it is apparent that decrease of potential to zero or even its reversal is in no way related, necessarily, to a decrease in stability or thickness of the interfacial layer, a condition precedent to coalescence, but, on the contrary, may be associated with a considerable increase in the stability of the interface. The present theory makes such phenomena understandable without the necessity for recourse to the theory of critical hydration or solvation conditions and is therefore a desirable simplification in dealing with colloids and emulsions.[24]

The theory of critical hydration, as well as critical potential conditions, as discussed by Kruyt,[24] shows that hydrophobe sols are sensitive to ion concentration, while hydrophile sols are insensitive to ion concentration but are sensitive to the action of dehydrating agents. In terms of the present theory, it is suggested that hydrophobe sols owe their stability to ion adsorption and therefore are sensitive to changes in ion concentration; while hydrophile sols owe their stability to molecular adsorption and therefore are insensitive to changes in ion concentration. Another way of expressing it would be that hydrophobe sols are more polar than the dispersion medium and adsorb ions and molecules (with their more polar ends turned toward the particle), hence such sols should be sensitive to changes in concentration of materials which furnish adsorbable materials of high polarity but which are "antagonistic" to the materials already at the interface. Hydrophile sols, on the other hand, would be less polar than the dispersion medium and would tend to adsorb its least polar constituents. They would, therefore, be sensitive only to changes in concentration of materials which furnish adsorbable materials of low polarity and which are "antagonistic" to the materials already at the interface.

Inasmuch as the previous discussion has considered the conditions of adsorption at free surfaces and at liquid-liquid interfaces and since the general

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[24] Kruyt: Alexander's "Colloid Chemistry," 1, 306 (1926).

problem of emulsions of necessity involves, in addition, the action of dispersed solids, it seems desirable to extend the discussion to a consideration of adsorption at liquid-solid interfaces.

The discussion of this condition, in terms of the present theory, is entirely analogous to the other two types of adsorption, with the single exception that there can be no appreciable alteration of the conditions on the solid side of the interface. Therefore, the adjustment of interfacial conditions must take place exclusively in the liquid phase. In adsorption at liquid-solid interfaces we must appreciate the two possibilities, as at liquid-liquid interfaces—i.e., the energy level in the solid is higher than in the liquid, in which case the more polar constituents of the liquid will be adsorbed; or the energy level in the solid is lower than in the liquid, in which case the less polar constituents will be adsorbed. The two cases are analogous to those just discussed in connection with hydrophobe and hydrophile sols. Two possible examples are polar silica and non-polar carbon.

As to the mechanism of action of dispersed solids in stabilizing emulsions, there seems no reason to alter the previously accepted concept of such action. This has been adequately discussed by Briggs,[25] Harkins,[26] Gortner,[27] Bartell and Osterhoff,[28] and many others. The only point which it may be worth while to mention here is to call attention to the very different interfacial conditions between the solid and each liquid, as compared to those between the two liquids. The situation of chief interest in emulsions is when the energy level of the solid plus its adsorbed film is between those of the liquids, as the solid then assumes a position in the interface. The problem, then, is to suitably alter the differential interfacial action so as to cause the removal of the solid from the interface and its dispersion in, for the case of petroleum emulsions, the water phase.

In a further effort to determine the degree of truth of the present theory, as regards adsorption of ions and molecules at the liquid-liquid interface, some experiments are in progress, in which natural emulsions are concentrated by gravity settling, the free oil and water removed and the residual emulsion resolved centrifugally. The characteristics of the several fractions are then determined. This work is still in its early stages, but some partial results can be reported at this time. The results are of interest in that they are analogous to those reported by Holmes for systems of known composition.[29]

Results on samples of two light-oil emulsions from the Texas Gulf Coast region are shown in Fig. 3, in which data on gravity, surface and interfacial tension, pH of brine and index of refraction are given. The additional tests at present contemplated are dielectric constants, conductivities, interfacial and phase boundary potentials, and magnetic permeabilities. It may be remarked that these samples were chosen for initial tests because it was be-

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[25] Ind. Eng. Chem., 13, 1008 (1921).

[26] Alexander's "Colloid Chemistry," 1, 192 (1926).

[27] "Outlines of Biochemistry," 154-156 (1929).

[28] Colloid Symposium Monograph, 5, 113 (1928).

[29] J. Phys. Chem., 29, 1205 (1925).

lieved that they might show minimum differences between the fractions and would therefore serve to indicate the adequacy of the test methods to show the expected differences. Also, these emulsions lend themselves very well to centrifugal resolution, on a laboratory scale, have no very volatile light ends and are statically quite stable.

Referring to Fig. 3, the columns headed "Free" refer to water and oil recovered by gravity settling; the columns headed "Centrif. Sepd." refer to the tightly emulsified components recovered by centrifugal resolution; while those headed "Chem. Sepd." refer to the oil from the residue of emulsion, which could not be resolved centrifugally and which had to be recovered by combined action of a suitable chemical and the centrifuge. In the latter case, the chemical used had a much lower index of refraction than the oil, so that the values for this fraction are probably somewhat low. The brine from the chemical resolution was not tested because it was known to contain a relatively high proportion of the chemical, which was water-soluble. In both cases, the amount of oil so recovered was too small for anything but refractive index tests. In sample No. 2 no free water settled out, so that but one sample of water, representative of the whole brine, was available. In all the work, every effort was made to prevent evaporation and contamination.

FIG. 3

Property	Sample No. 1		Sample No. 2	
	Free	Centrif. Sepd.	Free	Centrif. Sepd.
Oil—Sp. g. at 60°F.	0.8911	0.8933	0.8956	0.8956
Surface Tension (15 min)	29.1/72.2°	28.9/78.0°	29.3/71.0°	28.9/80.0°
Index of Refrac.	1.4925/70.9°	1.4935/72.0°	1.4913/83.5°	1.4923/83.8°
Brine—Sp. g. at 60°F	1.0728	1.0728		1.0792
pH	6.58	6.75		6.61
Surface Tension(15 min)	64.6/72.0°	59.9/78.0°		60.7/69.0°
Index of Refrac.	1.3502/67.3°	1.3502/69.3°		1.3514/84.2°
Interfacial Tension				
O—W 15 min.	20.9	15.3	18.7	15.6
W—O 15 "	6.0	6.7	16.4	8.5
IT diff. 15 "	+14.9	+8.6	+2.3	+7.1
Temp.	72.2°	78.0°	70.0°	78.8°

Index of Refrac.	Chem. Sepd.
Oil—Sample No. 1	1.4953/72.9
Sample No. 2	1.4959/84.2°
Chemical Agent	1.4811/74.5°

All temperatures in Fahrenheit degrees.

It will be observed that gravities and surface tensions of the oil fractions do not differ appreciably, but that index of refraction data indicate a progressive increase with "tightness" of emulsification. Similarly, the gravities and refractive indices for the brine fractions show no significant differences, while pH increases and surface tension decreases with "tightness" of emulsification. The interfacial tension values given are obtained, for an age of interface of fifteen minutes, by reading from curves of determinations extending over a period of thirty minutes and represent the time when the rate of change has, in most cases, fallen to a low value. Those values indicate a significantly higher interfacial tension (from oil to water) for the "free" components than for the "emulsified" ones. The data are given exactly as taken, without correction to standard conditions—except in the case of gravities,— as other temperature coefficients have not been determined.

The results seem to indicate an appreciable increase of concentration of polar materials in the tightly emulsified oil and an increase of (in this case) hydroxyl ions in the tightly emulsified brine, both of which observations are concordant with the requirements of the present theory. In this connection, it may be recalled that Dow[30] has already shown appreciable differences between the "free" and "emulsified" oil from natural emulsions.

With reference to natural oil-in-water emulsions, of which there are relatively few examples in this country, the principles of the present theory indicate that they should owe their stability primarily to ion adsorption from the external phase, modified by the effect of ionic and molecular adsorption on the inner (oil) side of the interface. The problem of oil-in-water emulsions is, to a great extent, the inverse of the water-in-oil problem.

The effects of temperature, particle size, dissolved or entrained gas, etc., which are often of importance in determining the formation and stability of emulsions, need only be mentioned as factors which alter the concentrations, energy relations, etc., of the primary solutions concerned.

The direct application, of the principles of adsorption here developed, to problems other than those of emulsions is so obvious as to hardly warrant its mention.

It will be remarked that the term "colloid" has not been employed in development of the present theory. There are several reasons for this apparent omission.

First, the term is an extremely indefinite one and leads to no very clear understanding of the mode of operation of "colloids" in stabilizing emulsions. Its use, therefore, would serve only to discourage a more critical search for the specific forces which must be operative.

Second, numerous attempts which have been made to demonstrate the presence of ultramicroscopically visible colloids in crude oils have failed entirely.[31] In this connection, Gurwitsch[32] calls attention to the very doubtful nature of the evidence which has been adduced to prove the presence of colloids in crude oils. Gurwitsch states:[33] "If, however, neglecting the cases of transition, we must define a typical colloidal solution, its most characteristic properties may be said to be; ultramicroscopic inhomogeneity and a capacity for spontaneous alteration of condition even with a constant concentration. . . ." He then proceeds to discuss the evidence under these headings and shows that it fails as proof of the colloidal character of crude oils. Although it is recognized that ultramicroscopic homogeneity is no absolute determination of non-colloidality, since the effects observed depend upon refractive index

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[30] Bur. Mines Bull., No. 250, 85-86 (1926).

[31] Zeiss cardioid ultra-microscope, with carbon arc, used in this work..

[32] "Petroleum Technology," 183-193 (1927), translated by Moore.

[33] "Petroleum Technology," 184 (1927), translated by Moore.

difference, nevertheless the failure of this method was another indication of the desirability of a change in point of view in studying emulsion problems.

Third, even though colloids do stabilize emulsions, they must do so by virtue of the physico-chemical properties of the substances composing the colloidal aggregates.

Fourth, the term colloid, as it is superfluous to remark, designates merely a state of subdivision of matter and has no necessary relation to the properties of that matter, whereas the efficiency of an emulsion-stabilizing material must certainly depend upon its specific molecular properties.

Fifth, the results of extensive research on petroleum emulsions have demonstrated the close relation between emulsion characteristics and ionic and molecular properties of the liquids composing the systems, whereas no systematic relation could be found on the assumption of a colloidal emulsifying agent of unknown composition and properties.

Sixth, it is known that suitable substances, whose particle sizes may range from molecular to macroscopic, are efficient in stabilizing emulsions.

Therefore, it is believed that, even in cases where the so-called emulsifying agent happens to exist within the size range designated as colloidal, the proper mode of attack is to consider the specific molecular properties of the constituents of the system and the changes of properties due to the particular state of aggregation of the several components, as they happen to exist at that time and in that system. The problem then resolves itself into the elements which have been discussed, plus a modification factor based on the state of aggregation. It is also believed, as has already been suggested,[34] that a useful application of the term "colloid" would be to the emulsion itself, rather than to some component of the system. In such an application, the dispersed phase, with its surrounding interfacial zone, would be considered the colloid. Such a point of view might bring out more clearly some of the reasons why, for example, an emulsion of extremely small particle size is so much more difficult to resolve than one of larger particle size. In fact, in emulsions of such small particle size that the droplets exhibit Brownian movement, it appears that much of the behavior is quite similar to what is observed in ordinary metal sols.

In view of all these factors, the decision was reached to forget "colloids" entirely and to try to describe emulsion systems in terms of the properties of ions and molecules and their behavior in non-homogeneous systems. The result of this decision is the theory which has been presented. In this connection, attention must be drawn to a publication of Fischer and Harkins,[35] relative to the characteristics of liquid-liquid interfacial films. They say, "The work already described proves definitely that: (1) the interfacial film which produces emulsification is not colloidal, and (2) it is not thicker than one molecule of the emulsifying agent, when the emulsifying agent is molecularly dispersed in its solution." Those findings are exactly in accordance with the

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[34] Gortner: "Outlines of Biochemistry," 10, 11, 33-42 (1929).

[35] J. Phys. Chem., 36, 109 (1932).

principles of the new theory and substantiate the wisdom of discarding the term "colloid" in dealing with emulsions.[36]

As will have been apparent in the course of this presentation, there is perhaps very little which can be considered as original, in the sense that it has never been said before. No claims of a high degree of originality are made, nor is it desired to appear to have employed the ideas of others without giving due credit.

The development of this theory was made necessary by the failure of prior theories consistently and properly to explain the observed facts in connection with petroleum emulsions.

The virtue of the theory, if any, does not necessarily rest upon its originality, but upon the degree to which it permits a relatively simple, consistent and complete explanation of the observed facts connected with the formation, stabilization and resolution of emulsions in general.

Thanks are due and are gratefully rendered to Dr. R. A. Gortner, University of Minnesota, for his helpful and sympathetic discussion and criticism of this theory and to members of the laboratory staff of the Petroleum Rectifying Company, especially Mr. R. L. Belshe, for invaluable assistance in experimental work and theoretical discussion.

Summary

1. A general definition of emulsions has been given and some of the prior emulsion theories have been briefly discussed.

2. The general properties of aqueous and non-aqueous solutions, in terms of ions and molecules, have been defined.

3. The application of known facts and accepted theories of physical chemistry to the problem of emulsification has been discussed.

4. The characteristics of adsorption of ions and molecules at free surfaces have been described.

5. The characteristics of adsorption of ions and molecules at liquid-liquid interfaces have been described.

6. Attention is drawn to the differences in adsorption conditions on the two sides of liquid-liquid interfaces.

7. Explanations of some of the observed characteristics of emulsion systems, which have not been satisfactorily explained by prior theories, are afforded by the present theory.

8. A restatement of the principal problems of emulsification, in the light of the present theory, is given; special reference being made to the particular problems of natural crude oil emulsions.

9. The mechanism of stabilization of an emulsion interface, in accordance with the principles of the new theory, has been described.

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[36] In connection with Harkins's paper (J. Phys. Chem., 36, 109 (1932)) it is suggested that the difference between his "expanded" and "condensed" films may be related to their ionic or molecular character.

10. The existence of and necessity for measuring the potentials and interfacial tensions on both sides of liquid-liquid interfaces has been discussed.

11. The measurement of interfacial tensions by the ring method, in which values are determined by pushing from oil to water, as well as, according to the conventional method, by pulling from water to oil, has been described and the possible meaning of the results discussed.

12. The independence of emulsion stability and interfacial potential is discussed.

13. A possible relation between hydrophobe and hydrophile sols and the principles of ionic and molecular adsorption is suggested.

14. The characteristics of adsorption of ions and molecules at solid-liquid interfaces have been described and the effect of solids at emulsion interfaces is discussed.

15. The partial results of separation and determination of the physicochemical properties of components of some natural emulsions have been presented as evidence of the validity of the new theory.

16. Natural oil-in-water emulsions are briefly discussed.

17. The concept of "emulsifying agents" as "colloids" has been critically discussed and the application of the term "colloid" to the dispersed phase, with its surrounding interfacial zone, is suggested.

Petroleum Rectifying Company of California,
Long Beach, California,
April, 1932.

SOME ASPECTS OF BOUNDARY LUBRICATION BY SOAP SOLUTIONS

BY ROBERT C. WILLIAMS

In the course of a study of lubrication as related to the process of drawing wire, some observations have been made which throw light on boundary lubrication in general. Boundary lubrication pertains to conditions accompanying the relative movement of bearing surfaces separated by relatively thin films of lubricant as distinct from thick, fluid film lubrication. High pressures which are localized at points of asperity are concomitant with boundary lubrication.

Wire-drawing is accomplished through the application of lubricants to the wire by various means. The condition of localized high pressures exists and lubricants vary greatly in their ability to facilitate drawing. Lubricants are generally applied in the form of mobile fluids (in which case they act also as coolants), greases or grease-like masses and powders, as for example soap powder. The present report is confined to the study of certain fluid lubricants, involving water as the continuous phase. Little if any fundamental published information exists on lubrication as related to wire drawing.

Experimental

The evaluation of the lubricant solutions was accomplished by drawing wire through a die and measuring the pull on the die or the "die pressure."

Fig. 1 illustrates diagrammatically the method employed. The wire, *A*, was pulled at constant speed through the die, *B*, in the direction indicated. The dynamometer plate, *D*, was in fixed position at the base and was deflected to the right during the drawing process.

The magnitude of the deflection was measured in thousandths of an inch by a dial gauge which was suitably mounted to make contact with the top of the plate, *D*. Various plates represented by *D* were calibrated so that a given deflection represented a pull of so many kilograms. The magnitude of the deflection depended on various factors, such as the size of wire drawn, percent reduction in cross-sectional area effected and so forth. By suitable choice among plates of different deflectability serious displacement of the die bearing from a straight line was avoided as the plate was deflected under load.

It was necessary to keep taut the wire to be drawn and a back pull was therefore provided. The magnitude and uniformity of the back pull influenced the pull on the die to a very marked extent. The wire to be drawn was taken from a spool mounted on a shaft. A pulley which served as a brake drum was mounted on the same shaft and a belt held taut against the pulley by two spring balances provided braking friction. The difference between the readings of the balances when the machine was operating gave the back pull on the wire.

The power for drawing was furnished by a one-quarter horse power A.C. motor which drove speed-reducing gears. A capstan, around which the wire was wrapped two or three times, was mounted on a shaft from the speed reducing gears. The wire was led off from the capstan to a friction driven take-up spool.

The speed of drawing was approximately 30 cm per minute in the experiments reported here. Under most conditions, at any rate, the pull on the die was found to be independent of the speed of drawing between the limits of 30 cm to 3900 cm per minute. This is in accord with the work of F. C. Thompson.[1]

It was essential that the wire be clean. This was accomplished through the use of organic solvents—acetone being perhaps the most useful. The development of chattering due to spasmodic seizure of the wire and the die while drawing indicated clean wire and a clean die bearing. Water exerted no lubricating action—chattering not being relieved through its use.

The lubricant solutions were applied by projecting a stream onto the wire and die approach. In the experiments reported here the wire was in contact with the lubricant for not more than two seconds before entering the die bearing as the wire was flooded for a distance of only about 0.5 cm in front of the die bearing. With clean uniform wire and with moderately homogeneous solutions (solutions which did not contain large macroscopic curds or aggregates of dispersed particles), consecutive reading did not vary more than plus or minus five per cent.

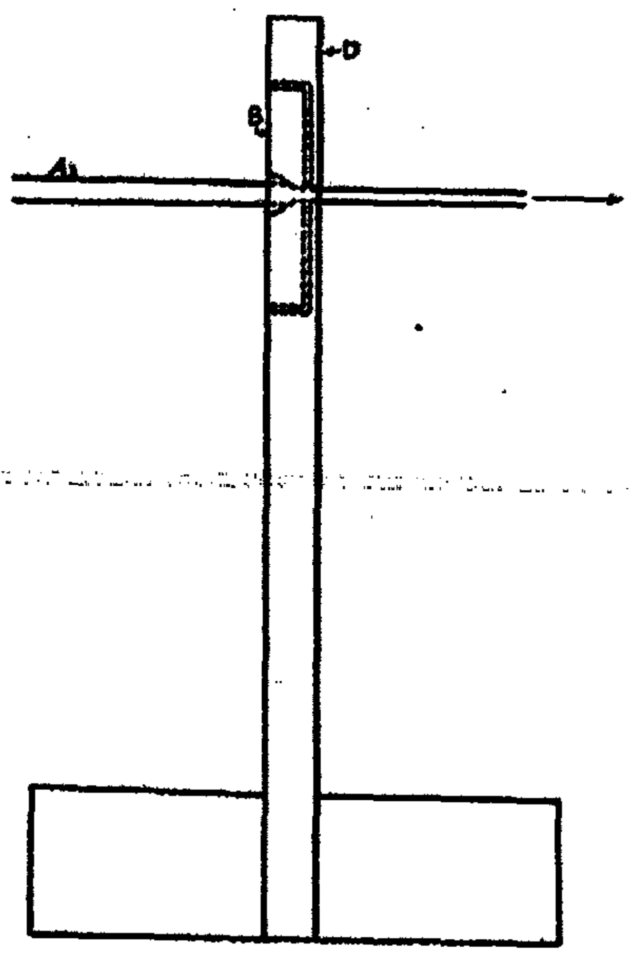

FIG. 1
Wire-Drawing Dynamometer

A Sodium Soap Solution as a Lubricant

Aqueous solutions of sodium or potassium soaps largely constitute or are commonly associated with lubricants for drawing copper wire. A fairly pure, commercial sodium soap of moderately high titre (40.8) was selected for several experiments. In all of the experiments reported here hard drawn copper wire having a diameter of 0.0242 inch was drawn through a 0.0225 inch tungsten carbide die at 30 cm per minute. The back tension on the wire was 1.8 kg. The experiments were carried out at room temperature and no attempt was made to exclude carbon dioxide from the air. Solutions having concentrations higher than 0.0072 *M* were not used as they were too gelatinous at room temperature. Surface tension was measured with the du Noüy tensiometer. pH was measured colorimetrically using Hellige Klett equip-

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[1] Sixth Sorby Lecture 10/10/30 pp. 1 to 24, Department of Applied Science, St. George's Square, Sheffield, Eng.

ment. Boiled-out distilled water was used in making up the solutions. The results obtained with solutions of this soap are presented in Tables I and II.

TABLE I

The Relation of Concentration to the Lubricating Effectiveness of a Sodium Soap

Mols per Liter	Percent Reduction in Pull on Die compared with Water* (Reduction means Increased Lubricating Efficiency)	pH of solution	Surface Tension of Solution in Dynes/cm.
0.0072	22	9.4	27.1
0.0036	22	9.4	26.7
0.0018	15	9.6	26.9
0.00082	11	9.3	26.9†
0.00041	11	8.7	29.7
0.000205	6	8.3	32.6

* With water seizure was experienced the pull on the die then being 9.1 kg. This held for all experiments reported here.

† The first reading at this point was 29.3, some time being necessary to reach the steady value of 26.9.

TABLE II

The Relation of pH to the Lubricating Effectiveness of a 0.0033M Solution of a Sodium Soap

pH of Solution*	Surface Tension of Solution in Dynes/cm.	Percent Reduction in Pull on Die compared with water
7.3	30.7	25†
8.6	27.1	23
9.5	26.9	22
11.7	34.7	19
12.1	34.7	15
12.4	34.9	0
12.7	34.7	0

* HCl was added to lower the normal pH, i.e. 9.5, and NaOH was added to obtain the higher values.

† Small particles of fatty acid or acid soap at pH 7.3 apparently made both the surface tension and die pull readings erratic.

As the concentration of the solution was decreased the effectiveness of the solution as a lubricant diminished rather sharply at a concentration neighboring that which first exhibited a definite increase in surface tension. This effect is presumed to be due to the incomplete formation of a film of lubricating material on the wire—the conditions supposedly being analogous to incomplete film formation at the air-water interface as indicated by the surface tension measurements. Had surface tension been measured by a dynamic method it is quite possible that the upward break in surface tension would have occurred at the same concentration as did the downward break in effectiveness of lubrication.

The pH data indicate the hydrolysis increased so rapidly with decreasing concentration that a maximum was reached. This increase in hydrolysis with dilution is in harmony with the work by McBain.[2]

A consideration of the constitution and behavior of soap solutions leads to an explanation of the rather surprising results given in Table II. In dilute soap solution the pronounced hydrolysis gives rise to free alkali, and accounts for the pH, fatty acid and acid soap. Addition of alkali repressed the hydrolysis, caused the disappearance of uncombined fatty acid and acid soap and decreased the lubricating effectiveness of the solution to zero. The equilibria in a soap solution system which are disturbed by the addition of alkali are given in Fig. 2. It was found that the addition of sodium chloride which, of course yields the common ion, sodium, exerted no such effect on lubrication at equivalent concentrations as did sodium hydroxide. Since the effect of the sodium ion in increasing the colloidal constituents was not responsible for the decreased lubrication it is apparent that fatty acid or acid soap was responsible for the lubrication by the soap solution.

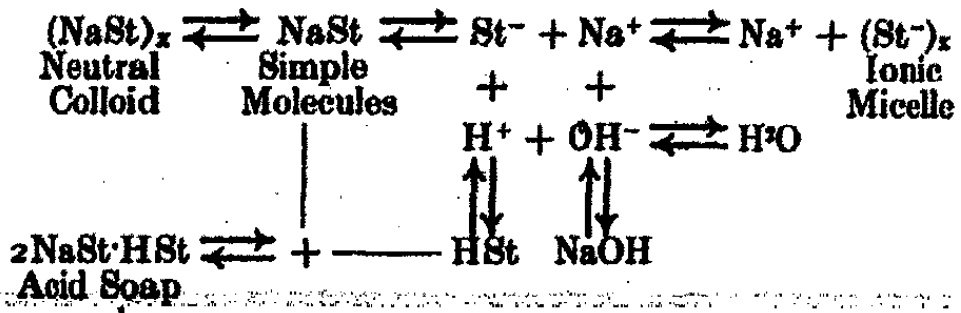

FIG. 2

Soap Solution Equilibrium Diagram (Sodium Stearate).

A Fat Emulsion as a Lubricant

Particularly striking were the results with an emulsion of tallow in a sodium soap solution which are presented in Tables III and IV.

TABLE III

The Relation of Concentration to the Lubricating Effectiveness of a Tallow-Sodium Soap-Water Emulsion

Concentration of Emulsion*	Percent Reduction in Pull on Die compared with Water	pH	Surface Tension of Solution in Dynes/cm.
2%	21	9.2	29.7
1%	21	9.4	31.1
0.5%	19	9.3	30.7
0.2%	19	9.2	31.4
0.1%	19	9.0	34.0
0.05%	15	8.5	37.3

* A concentrated emulsion was used which contained 60% tallow (free fatty acid content 0.5%), 20% sodium soap and 20% water. This was used in making the dilute emulsions, for example, 2 parts of the concentrate were used with 98 parts of water to make a "2% emulsion."

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[2] Bogue's: "Colloidal Behavior," 1, 410 (1924). (Good summary and bibliography.)

TABLE IV

The Relation of pH to the Lubricating Effectiveness of a 2% Tallow-Sodium Soap-Water Emulsion

pH of Solution	Surface Tension of Solution in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
6.8	27.8	25
9.2	29.7	21
11.7	33.2	17
12.1	35.4	16
12.4	35.4	9
12.7	35.8	0

It is noteworthy that the incorporation of tallow in the soap solution did not alter the trend of the results. Under the experimental conditions the relatively large proportion of tallow in the solution apparently played a comparatively minor rôle in the lubrication at the wire and die interface. Fatty acid or acid soap was apparently the factor upon which lubrication depended in this case also.

Triglycerides which are supposedly free from fatty acid possess definite lubricating value though they are markedly inferior to fatty acids. Wells and Southcombe,[1] in their important investigations, found that it was necessary to add to mineral oil 60 to 80% of rapeseed oil, which had been freed from fatty acids, to obtain the same degree of lubrication that was obtained by the addition of 1 to 2% rapeseed oil fatty acids.

The triglycerides in tallow, which should also possess lubricating value, did not apparently come into contact with the wire at high pH values at least.

An Ammonium Soap as a Lubricant

Tests similar to the above were carried out using solutions of ammonium linoleate. The results are presented in Tables V and VI.

TABLE V

The Relation of Concentration to the Lubricating Effectiveness of Ammonium Linoleate

Concentration in Mols* per Liter	pH of Solution	Surface Tension in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
0.0714	8.8	26.9	20
0.0357	8.8	27.4	22
0.01785	8.7	27.6	26
0.00714	8.6	27.6	28
0.00357	8.6	27.6	26
0.00179	8.4	29.2	23

* Given on basis of fatty acid since the ammonia volatilized somewhat.

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[1] Chemistry and Industry, 39, 51 T (1920).

TABLE VI

The Relation of pH to the Lubricity of a 0.00714 M Solution of Ammonium Linoleate

pH of Solution*	Surface Tension in Dynes/cm.	Percent Reduction in Pull on Die compared with Water
8.6	27.6	28
9.3	27.4	25
9.5	27.6	22
9.6	27.6	19
9.8	27.4	19
10.0†	27.6	19

* Ammonia was added to increase the pH.
† This solution was not at all turbid.

It is well known that ammonium soaps hydrolyze to a much greater degree than do sodium or potassium soaps except in the very dilute range where both hydrolyze almost completely. Ammonium hydroxide, being a weak base, produced a comparatively low degree of alkalinity in the solutions. As the concentration of the soap was decreased the alkalinity remained remarkably constant.

It is believed that the physical state (degree of peptization) of the fatty acid particles is a factor which, in part, accounts for the maximum lubricating effectiveness of the 0.00714 M solution. Subsequent work on emulsions having particles of different ranges in size has given weight to this belief. The experiments involving the deliberate variation in pH are in harmony with the preceeding analogous experiments with the other solutions. When the pH of the ammonium linoleate solution was markedly increased by the addition of sodium hydroxide the effect on lubrication was the same as previously.

The well-known work of Sir W. B. Hardy and his collaborators[4] shows the importance of fatty acids and other long chain polar compounds in lubrication. Although soap is an example of this type of compound the evidence presented here showed that soap solutions free from fatty acid do not possess lubricating properties. The X-ray studies by Trillat[5] indicate that fatty acid molecules are approximately perpendicularly oriented at the surfaces of solids with the COOH group turned towards the solid. With certain metals the nature of the spectrum at the metallic surface was such that it could be distinguished from the fatty acid spectrum. This difference was attributed to a combination of the fatty acid with the metal. It seems reasonable that in accordance with Trillat's experiments, fatty acids would be much more readily adsorbed by metals than a soap, such as a sodium soap, which is itself the result of the combination of a fatty acid and a metal.

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[4] Alexander's "Colloid Chemistry," 1, Chap. 13 (1926). Chapter including bibliography by Hardy.

[5] Compt. rend., 180, 1838 (1925); Metallwirtschaft, 7, 101 (1928); 9, 1023 (1930).

Summary

An apparatus has been devised for the study of lubricants and lubrication as related to wire drawing in particular.

The lubricating effectiveness of sodium and ammonium soap solutions was due to the products of hydrolysis, fatty acid or acid soap.

When hydrolysis was sufficiently repressed lubrication by soap solutions was entirely lacking.

When fat (tallow) was emulsified in a soap solution, lubrication was not appreciably affected at low or high pH values.

No parallelism existed between the lubricating effectiveness and the surface tension of the solutions when the pH was varied. However, as the concentration of a given solution was decreased to a point neighboring that at which the lubricating effectiveness diminished rather sharply the surface tension increased.

There was an indication that the degree of peptization of the fatty acid or acid soap was a factor in lubrication by soap solutions.

Acknowledgment

The writer wishes to express his thanks to the Ironsides Co. and to the Battelle Memorial Institute for permission to publish this work.

The writer is particularly indebted to Drs. H. W. Russell and O. E. Harder of the Institute staff for their aid and encouragement.

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3115

ADHESION TENSION

A Receding Contact Angle, Pressure of Displacement Method

BY F. E. BARTELL AND CHARLES E. WHITNEY

During the past five years a number of investigations have been reported in which adhesion tension values of certain solid-liquid systems have been obtained. In nearly all of these investigations the original pressure of displacement method of Bartell and Osterhof[1] was used. With this method finely divided solid material is compressed into a membrane. Liquid is brought into contact with this membrane and the pressure is measured which is just sufficient to prevent movement of liquid through its pores. At the very beginning of the experiment liquid is allowed to advance, but very shortly thereafter further advance is prevented by gradually building up an opposing pressure. Advance of liquid is detected by noting movement of liquid in the indicator tube attached to the low pressure side of the system.

At the time of the original pressure of displacement work it was assumed that one and only one definite equilibrium contact angle was possible for any given solid-liquid-air (or solid-liquid-liquid) system. The existence of advancing and of receding angles was well known, but it was assumed, at least by us, that either an advancing or a receding angle would, within a short time, so adjust itself as to give finally a definite equilibrium angle which would be the same whether approached from the advancing or the receding angle. We have since obtained good evidence that advancing angles and receding angles may each exist as definite, but different, equilibrium angles. A careful consideration of the precise method used in the earlier work led us to believe that the periodic increases in pressure imposed upon the system gave a final pressure which in nearly every case was ascribable to the effect of the receding equilibrium angle; we could not be absolutely certain, however, that this was actually the case.

Somewhat over two years ago an attempt was made in our laboratory to construct an apparatus with which a liquid system advancing by capillarity within the pores of the membrane would automatically build up a pressure which would reach a maximum value and would then serve as a measure of the balancing or equilibrium pressure. Throughout the operation of this method the contact angle would at all times be of the advancing type. At present we need state only that much difficulty was encountered in our attempts to obtain reproducible values. The details of this work will be presented in another paper. A still later investigation on contact angles, in our laboratory (unpublished), has shown that receding angles are more easily reproducible than are advancing angles. In view of the above findings it was decided to carry

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[1] Bartell and Osterhof: Colloid Symposium Monograph, 5, 113 (1927); Ind. Eng. Chem., 19, 1277 (1927); Z. physik. Chem., 130, 715 (1927); J. Phys. Chem., 34, 1399 (1930).

out an investigation in which the displacement pressure apparatus would be so operated that receding contact angle measurements would of certainty be obtained. In carrying out this plan the membrane pores were first completely filled with liquid and then the minimum pressure required to force back the liquid column was determined.

Experimental

Apparatus.

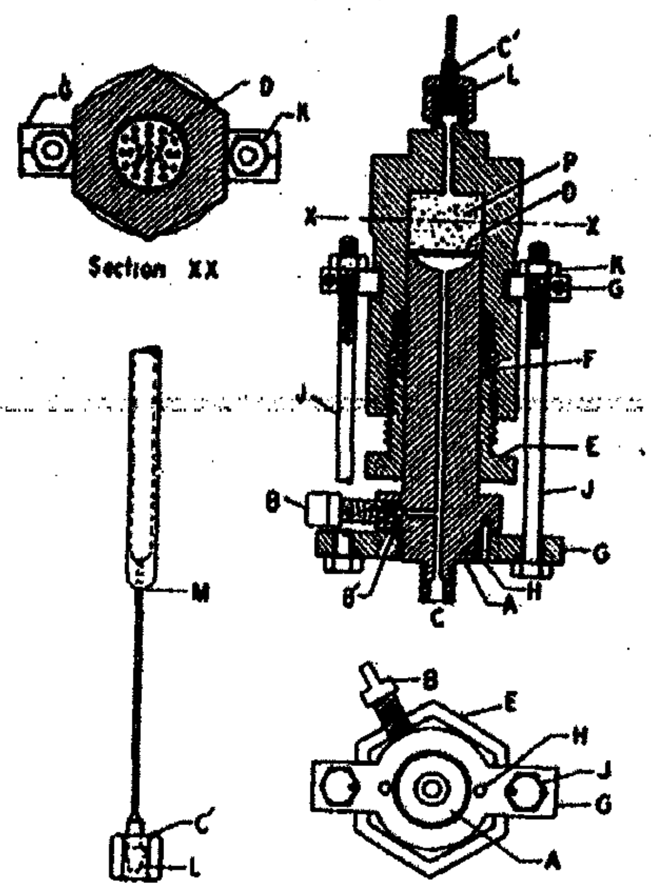

Fig. 1
Assembly and Details of Cell

Displacement Cell. An assembled cell and its parts are shown diagrammatically in Fig. 1. The cells were similar in construction to those used by Bartell and Osterhof.[1] They were shorter, the chamber being about 23 mm in length; one end was solid except for a small outlet to which a connection was made with a manometer. A glass capillary indicator tube was attached to the other end of the cell.

Manometer. The manometer was of the simple U-tube type with an auxiliary or third arm. One arm of the manometer was of 7 mm glass tubing. This was sealed to a ground-glass joint by means of which connection was made with the cell. The second arm was a capillary tube in which the mercury level was regulated and observed. The third or auxiliary arm was joined to the bottom of the U-tube next to the capillary arm. It was provided with a stopcock with which it could be shut off from the rest of the manometer. The main purpose of this third arm was to serve as a reservoir making possible a gradual lowering of the mercury in the capillary tube. At the lowest part of the manometer was a capillary outlet consisting of a stopcock and a drawn-out tip. This outlet was for the purpose of removing mercury slowly in order to bring about a gradual decrease of pressure within the manometer system. The connection from the manometer to the cell consisted of a ground glass joint above which was a 3-way stopcock. Above the stopcock was a small bulb and beyond this was a copper tube attached to a small union *C*, *C'*, *L* (Fig. 1) with which final connection was made.

Packing Apparatus. A method was developed for packing a powder into the form of a membrane so that a given amount of either wet or dry powder might be used and give essentially the same volumes.[2] The packing or tamping machine used for packing the powder in the the cell was developed by Bartell and Jennings.[2] Briefly, it consisted of a packing plunger 2.5 kilograms in weight which was raised by turning a crank and caused to fall on

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[2] Bartell and Jennings: unpublished.

the powder in the cell. A suitable device held the cell in position and kept the plunger in alignment during its fall. The apparatus was adjusted so as to allow the plunger to fall a distance of 85 mm.

Thermostat. The experimental determinations in this work were all carried out in an air thermostat at 25°C. The temperature was controlled to within 0.1°C.

Materials.

Silica. The only solid used in this work was silica, a ground Ottawa sand of fairly high purity. It was twice treated with boiling 1:1 HCl, then with hot water and filtered. The silica was then washed with boiling water about twenty times. It was dried in an oven at 100°C and muffled at red heat for about 2 hours. It was graded by sieving, about three-fourths of it passed thru at 350 mesh, the remainder was discarded. This screened powder contained not only particles which would just pass thru the sieve but also much very fine powder which if shaken up with water would not settle out for several days. Such variation of particle size was not desirable as the pore size of the compressed membranes formed with it would not be uniform. In order to obtain a smaller range of particle size, the silica which had passed thru the 350 mesh sieve was stirred up in a large crock of distilled water and was allowed to settle for 30 minutes. The suspension which had not settled out was siphoned off and the settled powder was carried thru this sedimentation process again. The settled powder was then dried and again muffled at red heat for 2 hours.

A test was made to determine whether the surface tension of liquids would be altered by standing in contact with this silica. Some of it was shaken with pure water. After removal of the silica by centrifuging, there was no change in the surface tension of the water. This indicated absence of water soluble impurities in the silica.

Liquids. All of the liquids used in this work were of good grade, though not of "highest purity." Determinations of the surface tensions of the liquids gave values which were in good agreement with accepted values.

Experimental Procedure.

Packing. The cell was placed in the packing apparatus. A small circular piece of linen cloth was placed in the bottom of the cell. This was to prevent silica being forced or blown out of the cell by the fall of the packing plunger upon the silica. Approximately 1 gram of silica was placed in the cell and a piece of cloth inserted on top of it. The silica was then subjected to 50 impacts of the plunger. About 6 one-gram increments of silica were used for the preparation of the membrane. The top cloth was removed before each addition of silica and then replaced for each packing operation.

Measurement of Pressure and Determination of Pore Size. After a cell had been packed it was assembled as shown in the diagram in Fig. 2. The liquid (a liquid which forms zero contact angle with the solid) was then drawn into the cell so as to wet the membrane completely. The tube connecting to the manometer was filled with liquid as far as the stopcock. It was then joined to the cell by means of the union. The cell was set up as shown in Fig. 1, and the connection to the manometer made by means of the ground-glass joint. The mercury level in the manometer was raised until mercury filled the 3-way stopcock. This stopcock was turned so as to make direct connection between the mercury and the liquid which extended into the cell. The mercury and liquid interface was then raised by loosening the valve, (*B* of Fig. 2), and raising the mercury level in the manometer. In this way the level of this interface was raised into the small bulb. Correction was made for the capillary depression of mercury in the capillary as well as for the liquid column which extended from the mercury level in the bulb to the cell. Since the final "negative" pressure was measured by the difference in the levels of the mercury in the bulb and in the capillary these corrections could be made simultaneously by noting the difference in levels of the two mercury meniscii when the valve, *B*, was open, or in other words when both columns were open to the air. After making this reading the valve was tightly closed. The indicator tube was then connected to the other end of the cell. A column of colored liquid was placed in this indicator tube to show when movement of the liquid in the cell occurred. The cell and manometer thus assembled were ready for the determination of the displacement pressure.

With the auxiliary arm of the manometer in direct connection, the outlet tube at the bottom of the manometer was partially opened. This was adjusted so as to give a very gradual lowering of the mercury in the capillary and auxiliary tubes. The pressure differential was thus increased slowly until the liquid in the indicator tube began to move. The pressure was then allowed to remain constant for a few minutes until the indicator liquid again became stationary. This procedure was repeated until the liquid showed a continuous movement in the cell towards the manometer. The success of the measurement is dependent upon a sufficiently slow and careful increase in the pressure differential. The pressure differential (*i.e.*, "negative pressure") which caused the continuous movement of the liquid was regarded as the equilibrium displacement pressure corresponding to the receding contact angle. Strictly speaking, this pressure was that required to draw air into the liquid-filled pores rather than the pressure required to prevent the displacement of air from the pores by the liquid. The small movements of the liquid which occurred before the maximum or equilibrium pressure was reached were attributed to displacement of the liquid from the linen disc at the end of the membrane and also to variations in the pore radii of the membrane. A pressure less than the equilibrium pressure was sufficient to initiate movement in a few large pores and this movement continued until smaller pores were reached. The movement of the liquid became continuous when the maximum pressure for the effective pore radii was reached, for at this pressure the liquid was probably moving in practically all of the larger pores.

A similar method was tried out in which the pressure was positive, *i.e.*, pressure was built up by increasing the mercury head on the high pressure side of the system. The pressure was measured which was just sufficient to drive liquid through the membrane. The results thus obtained give good agreement with those reported herein. The "pull method" is limited in use to systems in which the displacing pressure is not greater than atmospheric pressure.

From the maximum (equilibrium) pressure values obtained the pore size was calculated by the equation,

$$r = \frac{2S}{hdg} = \frac{2S}{Pg}{}^{*}$$

Data obtained in measurement of pore size of the silica membranes used are given in Table I.

TABLE I

Determination of Pore Size of Compressed Silica Powder Membranes

System	P grams/cm²	S dynes/cm	r × 10⁻⁴cm
Water—Air—Silica	469	72.08*	3.13
Water—Benzene—Silica	229	34.76**	3.10
Water—Nitrobenzene—Silica	166	25.32**	3.10
		Average	3.11

* Surface Tension
** Interfacial Tension

It might be mentioned that Bechhold,[3] and Bigelow and Bartell,[4] as well as others have measured pore radii of porous membranes by determining the pressure required to force liquid out of the pores. In principle that method and this one are essentially the same.

We found it possible to measure pore size by means of liquid-liquid as well as liquid-air systems. Bartell and Greager[5] measured interfacial tensions by a displacement pressure method in a porous membrane of calcium fluoride. Bechhold and Schnurmann[6] have also used liquid-liquid systems to measure pore size of porous membranes and found that the values agree closely with those obtained with liquid-air systems. In carrying out similar measurements in this work the compressed membrane was first wetted completely with water and the water-organic liquid interface was then drawn into the pores. The pressure required to prevent displacement of the organic liquid by the water was then measured.

Determination of Adhesion Tension of Contact Angle Forming Liquids. The determination of the adhesion tension of liquids, which in contact with air

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[*] The symbols used in this paper are the same as those used in recent publications from this laboratory, namely: S_1 = Surface tension or free surface energy of solid phase; S_2 = Surface tension or free surface energy of liquid phase; S_3 = Surface tension or free surface energy of water.

A combination of subscripts refers to interfacial tension values as S_{23} = interfacial tension of organic liquid against water, S_{12} = interfacial tension of organic liquid against solid, etc. θ represents the angle of contact, P represents the displacement pressure, and g represents the gravitational constant.

[3] Z. physik. Chem., 64, 328 (1908).

[4] J. Am. Chem. Soc., 31, 1194 (1909).

[5] Unpublished work completed in May, 1929.

[6] Z. physik. Chem., 142, 1-24 (1929).

form contact angles with silica, was readily carried out by measuring the contact angle formed in each case. The membrane was completely wetted with the contact angle forming liquid, the cell and manometer set up, and the pressure differential increased until the liquid started to be pulled back through the cell. (The pressure at which this occurred was lower than that corresponding to the force of surface tension of the liquid and the extent of this lowering is directly related to the magnitude of the receding contact angle.) The auxiliary arm of the manometer was then shut off from the capillary by means of the topcock provided for that purpose, the mercury in the capillary began to rise as the liquid within the membrane receded. After a period of time this movement ceased and the liquid became stationary as did the mercury column in the manometer. The pressure remained constant at that point for several hours. This pressure value was quite reproducible and was considered to be representative of the receding equilibrium contact angle. The contact angle was calculated by use of the equation,

$$\operatorname{Cos}\theta = \mathrm{rPg}/2\mathrm{S}. \qquad (2)$$

The adhesion tension, A_{12}, of the contact angle forming liquid was calculated by use of the equation,

$$A_{12} = S_2 \cos\theta, \qquad (3)$$

or from the more general equation,

$$A_{12} = S_2 K,$$

in which K may be considered as the adhesion constant which may have a value greater than unity. Adhesion tension values were determined for five liquids which form contact angles against silica and are to be found in Table II.

TABLE II

Adhesion Tension Determinations of Contact Angle-Liquids
Organic Liquid—Air-Silica

$r = 3.11 \times 10^{-4}$cm

	P grams/cm²	θ	cos θ	S_2 dynes/cm	A_{12} dynes/cm
Acetylene tetrabromide	281	29°25′	0.874	49.07	42.8
Alpha Brom-naphthalene	260	25°43′	0.901	44.00	39.6
Alpha Chlor-naphthalene	256	18°44′	0.947	41.20	39.0
Bromoform	245	23°56′	0.914	40.93	37.4
Iodobenzene	243	18°00′	0.951	39.10	37.2

Determination of the Adhesion Tension of Water. The adhesion tension of water against silica was determined by the measurement of the contact angles formed by liquid-liquid-solid systems. The organic liquid used was one which forms a contact angle with silica and whose adhesion tension against silica had been measured as previously described. The determination of the interfacial contact angle formed by the water-organic liquid interface against silica required a slightly different procedure from that used for the determination of the solid-liquid-air angles previously described. The compressed powder membrane was wetted completely with the contact angle forming liquid and then a small increment of silica wetted with water was packed on top of the silica wetted with the organic liquid. The cell was then assembled and set up as in previous measurements. The pressure differential was increased slowly within the system until movement of the liquids in the cell ceased. When this occurred the auxiliary arm of the manometer was shut off as in the previous determination and the system allowed to attain equilibrium. This was assumed to have been reached when the pressure differential was so great that there was no more displacement of the organic liquid by the water. The interfacial contact angle was then calculated by means of the equation,

$$\mathrm{Cos}\ \theta_{23} = \mathrm{rPg}/2\mathrm{S}_{23}. \qquad (4)$$

Since the adhesion tension, A_{12}, of the contact angle forming liquid was known and the value of the contact angle of the interface likewise known, the adhesion tension, A_{13}, of water against silica was calculated by means of the equation,

$$\mathrm{A}_{13} = \mathrm{A}_{12} + \mathrm{S}_{23} \cos \theta_{23}. \qquad (5)$$

Five separate determinations of the adhesion tension of water against silica were carried out using water with each of the five contact angle forming liquids previously mentioned. These results are to be found in Table III.

Determination of the Adhesion Tension of Zero Contact Angle Liquids. The determination of the adhesion tension of organic liquids which form a zero contact angle with silica was carried out by the measurement of interfacial contact angles. In this case, however, the adhesion tension of water was known and the adhesion tension, A_{12}, of these organic liquids was calculated by equation (5). The procedure used in obtaining the interfacial contact angles was practically the same as in the last case mentioned, the only difference being the use of organic liquids which form zero contact angles with silica in place of the ones which form finite angles. Thirteen such organic liquids were used. Eight of them had been used in previous investigations but were used in this work so that the results might be compared with those obtained by other methods. The results are given in Table IV.

TABLE III

Adhesion Tension Determinations of Water against Silica By Measurement of Interfacial Contact Angles

(Water—Organic Liquid—Silica)

	P grams/cm^2	θ_{23}	cos θ_{23}	S_{23} dynes/cm	A_{13} dynes/cm
Acetylene tetrabromide	221	28°29′	0.879	38.32	76.4
Alpha Brom-naphthalene	242	27°15′	0.889	41.57	76.6
Alpha Chor-naphthalene	245	21°52′	0.928	40.24	76.3
Bromoform	261	9°15′	0.987	40.35	77.2
Iodobenzene	260	16° 3′	0.961	41.34	76.9
				Average	76.7

TABLE IV

Adhesion Tension Determinations of Zero Contact Angle Liquids against Silica

Water A_{13} = 76.7 dynes/cm. K = 1.07
Water—Organic Liquid—Silica
$r = 3.11 \times 10^{-4}$ cm

	P grams/cm²	θ_{23}	cos θ_{23}	S_{23} dynes/cm	S_2 dynes/cm	A_{12} dynes/cm	K*
Butyl acetate	79.8	22°20′	0.925	13.2	24.1	64.5	2.68
Nitrobenzene	125	41°25′	0.750	25.3	43.3	57.7	1.33
Chloroform	192	22°11′	0.926	31.6	26.5	47.4	1.79
Benzene	215	19°16′	0.944	34.7	28.2	44.1	1.56
Toluene	221	21°57′	0.928	36.5	28.1	43.2	1.54
Carbon disulfide	226	44°16′	0.716	48.1	31.2	42.3	1.34
Ethyl benzene	233	22°20′	0.925	38.4	28.5	41.2	1.45
Chlorbenzene	240	15°36′	0.963	37.9	32.6	40.2	1.23
Propyl benzene	241	23°13′	0.919	40.0	28.6	40.0	1.40
Brombenzene	245	19°20′	0.944	39.6	35.9	39.3	1.09
Butyl benzene	249	24° 3′	0.913	41.6	28.8	38.7	1.34
Carbon tetrachloride	265	24°46′	0.908	44.5	26.1	36.3	1.39
Hexane (synthetic)	333	4°35′	0.997	51.0	18.2	25.9	1.42

* $K = A_{12}/S_2$ (or $A_{12} = KS_2$)

Discussion of Results

In Tables V and VI are given adhesion tension values for a series of liquids against silica obtained by the original pressure of displacement method,[1] values obtained by the single transparent capillary tube method,[7] and values obtained by the present "receding contact angle pressure of displacement" or so-called "pull" method.

Reasonably good agreement is noted throughout for the adhesion tension values of contact angle forming liquids listed in Table V. The adhesion tension values obtained for water against silica show good agreement for the single capillary method and the "pull" method, the average values being 75.8 and 76.7 dynes/cm, respectively. The corresponding value obtained with the original pressure of displacement method was 81.5 or about 6 dynes/cm higher. This difference in values can be attributed to one of two things, either (1) the free surface energy of the silica (tripoli) used in the original investigation was different from that of the fused quartz and the sand of the other investigation, or (2) the higher value for the adhesion tension of water obtained in the original investigation was due to experimental errors in that work. The value obtained was dependent upon results of work with one contact angle forming liquid only, namely, alpha bromnaphthalene. An error in the determination of the interfacial contact angle of alpha bromnaphthalene against water would account for the difference in values obtained. This work

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[7] Bartell and Merrill: J. Phys. Chem., 36, 1178 (1932).

TABLE V

Comparison of Adhesion Tension Values obtained by Different Methods
Contact Angle Forming Liquids against Silica

	Original Pressure Method A_{12}	Single Capillary Method A_{12}	Present Method A_{12}
Acetylene tetrabromide		43.3	42.8
Alpha Brom-naphthalene	41.1	41.1	39.6
Alpha Chlor-naphthalene		39.8	39.0
Bromoform		37.3	37.4
Iodobenzene		38.2	37.2

Water against Silica

(Water—Organic Liquid—Silica System)

	A_{13}	A_{13}	A_{13}
Acetylene tetrabromide		76.3	76.4
Alpha Brom-naphthalene	81.5	75.9	76.6
Alpha Chlor-naphthalene		76.2	76.3
Bromoform		75.3	77.2
Iodobenzene		75.5	76.9
Average	81.5	75.8+	76.7

has been rechecked and we have no good evidence of any error in the original work. It seems then that the most logical conclusion is that the original silica used (tripoli) possesses surface properties different from those of fused quartz and of sand.

In Table VI are given adhesion tension values obtained by each of the three methods for a series of organic liquids against silica. Again it is noted that good agreement was obtained with the single capillary method and the

TABLE VI

Comparison of Adhesion Tension Values obtained by Different Methods

Zero Contact Angle Liquids against Silica
Water—Organic Liquid—Silica

	Previous Pressure Method	Single Capillary Method	Present Method
Butyl acetate	72.1	66.6	64.5
Nitrobenzene	61.4	57.3	57.7
Chloroform	58.7	45.4	47.4
Benzene	51.2	46.5	44.1
Toluene	53.4	46.5	43.2
Carbon disulfide	43.2	40.5	42.3
Carbon tetrachloride	39.5	35.6	36.3
Hexane (synthetic)		29.9	25.9

"pull" method while the values obtained with the original method are uniformly higher. These higher values are to be expected if one considers that the values obtained for each of these liquids is dependent upon the value for water used in the calculation.

Were the value of 76 to be accepted as the adhesion tension value for water against tripoli (as it appears to be for the other forms of silica), then the adhesion tension values for the other liquids against it would be practically the same as obtained for them against fused quartz and sand. As above stated we have no good reason to believe that the earlier work is seriously in error, so we shall conclude for the present that the surface properties of the different forms of silica are different. This latter view appears to be justified from more recent work in this laboratory which is as yet unpublished in which it has been shown conclusively that the surface properties of surfaces such as of silica are dependent upon the precise treatment to which they are subjected.

Work of Adhesion. Water vs. Solid Surfaces against a Series of Organic Liquids. It was found by Bartell and Hershberger[8] that decreases in free surface energies which occur when a polar solid and each of a series of liquids are brought together are in the same direction and of the same relative magnitude as the decreases which occur when the same series of liquids are brought into contact with water. Harkins and Dahlstrom[9] have observed that: "the energy relation at the interface between solid oxides and organic liquids are similar to those between water and the same organic liquids."

The data obtained in the present work tends to substantiate these generalizations and has shown further *a definite relationship between the work of adhesion of a series of organic liquids for silica and for water.* The work of adhesion, W_a, represents the change in energy (ΔF) which occurs when a given phase, as a solid, comes in contact with a liquid, *i.e.*,

$$\Delta F = W_a = S_1 + S_2 - S_{12}. \qquad (6)$$

Similarly when an organic liquid surface and a water surface come together the free surface energy relations may be expressed as follows:

$$\Delta F' = W_a' = S_3 + S_2 - S_{23}. \qquad (7)$$

The free surface energies of a solid-air or of a solid-liquid interface are not determinable but the decrease in free surface energy which occurs when a solid-air interface is replaced by a solid-liquid interface is represented by the adhesion tension of the liquid against the solid. It is therefore permissible to use the following equation:

$$\Delta F = W_a = A_{12} + S_2. \qquad (8)$$

By the substitution of appropriate data in equation (8), the work of adhesion of an organic liquid against silica can be calculated. Such calculations were made for all the organic liquids used in this work and the results are given in Table VII. Similarly from equation(7), the work of adhesion of these same

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[8] Ind. Eng. Chem., 22, 1304 (1930).

[9] Ind. Eng. Chem., 22, 897 (1930).

organic liquids against water was calculated. Also the ratios of the work of adhesion of the organic liquids against silica to the work of adhesion of the same liquids against water were calculated and are given in the last column of Table VII.

TABLE VII

Comparison of the Work of Adhesion of Organic Liquids against Silica and of the Same Liquids against Water

Organic Liquid against Silica: $W_a = S_1 - S_{12} + S_2$ or $W_a = A_{12} + S_2$
Organic Liquid against Water: $W_a' = S_3 - S_{23} + S_2$. ($S_3$ = 72.1 ergs.)

	Organic Liquid against Silica			Organic Liquid against Water			
	A_{12} ergs	S_2 ergs	W_a ergs/cm²	S_{23} ergs	S_3-S_{23} ergs	W_a' ergs/cm²	W_a/W_a'
Nitrobenzene	57.7	43.3	101.0	25.3	46.8	90.1	1.12
Acetylene tetrabromide	42.8	49.1	91.9	38.3	33.8	82.9	1.11
Butyl acetate	64.5	24.1	88.6	13.2	58.9	83.0	1.07
Alpha Brom-naphthalene	39.6	44.0	83.6	41.6	30.5	74.5	1.12
Alpha Chlor-naphthalene	39.0	41.2	80.2	40.2	31.9	73.1	1.10
Bromoform	37.4	40.9	78.3	40.4	31.7	72.6	1.08
Iodobenzene	37.2	39.1	76.3	41.3	30.8	69.9	1.09
Brombenzene	39.3	35.9	75.2	39.6	32.5	68.4	1.10
Chloroform	47.4	26.5	73.9	31.6	40.5	67.0	1.10
Carbon disulfide	42.3	31.3	73.9	48.1	24.0	55.6	1.33
Chlorbenzene	40.2	32.6	72.8	37.9	34.2	66.8	1.09
Benzene	44.1	28.2	72.3	34.6	37.5	65.7	1.10
Toluene	43.2	28.1	71.3	36.1	36.0	64.1	1.11
Ethyl benzene	41.2	28.5	69.7	38.4	33.7	62.2	1.12
Propyl benzene	40.0	28.6	68.6	40.0	32.1	60.7	1.13
Butyl benzene	38.7	28.8	67.5	41.6	30.5	59.3	1.14
Carbon tetrachloride	36.3	26.1	62.4	44.5	27.6	53.7	1.16
Hexane	25.9	18.2	44.1	51.0	21.1	39.3	1.12

From this table it can be seen that the relative order of decrease in the values of the work of adhesion from liquid to liquid in a series of organic liquids is the same in the case of both silica and water. From the obtained ratio, W_a/W_a', it is to be noted that the values representing free surface energy changes must be of the same order for silica and water since the ratio obtained is quite close to unity.

Conclusions which can be drawn from this investigation are that the receding contact angle pressure of displacement method is comparatively rapid, the results are duplicable and the adhesion tension values calculated from the data obtained with this method are reliable adhesion tension values for the systems in question.

Summary

1. A pressure of displacement method was developed for the measurement of receding contact angles formed within the pores of a membrane of compressed powder. The time required to reach a final characteristic pressure value was much shorter than with methods previously used.

2. The adhesion tension values for water against silica calculated from data obtained by this method agree closely with values obtained by the single capillary method. They are about 6 dynes/cm lower than the values obtained by the previous pressure of displacement method.

3. The adhesion tension values and the contact angle values obtained by this method for liquids which form contact angles with silica are in close agreement with values obtained by the single capillary method.

4. The adhesion tension values of various organic liquids (including zero contact angle forming liquids) against silica determined in this work agree closely with those obtained with the single capillary method and are consistent with those obtained in previous displacement pressure work.

5. The adhesion tension values against silica of several organic liquids not previously used have been determined.

6. Further evidence has been obtained that the free surface energy changes which occur when given organic liquids come in contact with polar solids are of the same relative order as the corresponding energy changes which occur when these same liquids come in contact with water. The ratio of the work of adhesion of an organic liquid with silica, W_a, to the work of adhesion of the organic liquid with water, W_a', is a constant whose value is close to unity (ave. value = 1.1+).

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ALUMINA LAKES*

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Reinmuth and Gordon[1] have prepared what they claim to be the aluminum salt of Orange II acid by several methods. Since many alumina lakes are adsorption complexes and not definite chemical compounds, it seemed desirable to make a phase rule study of the alumina lakes of alizarin and Orange II. The Orange II was furnished us through the courtesy of the duPont Company. The free acid was prepared by the method of Sisley.[2] Orange II acid is soluble enough in water to be used that way; but alizarinic acid must be used in alcoholic solution.

Powdered alumina from Kahlbaum has been calcined and is quite inert to acids. It took up no alizarinic acid from alcoholic solution and did not react with Orange II in aqueous solution. Sulphuric acid (1-20 N) had no action on it in one week. An alumina catalyst was prepared by heating aluminum nitrate in the usual way. It was only colored a faint pink after standing for a week in contact with a saturated solution of alizarinic acid in alcohol.

Alumina was then precipitated from aluminum chloride with a slight excess of ammonia. The precipitate was washed five times by decantation, filtered, and dried partially between filter paper. It was then suspended in sufficient alcohol to form a thick suspension, which was filtered through cheese-cloth to give uniformity. This suspension was evaporated to dryness and the solid heated in an oven at 110° for forty-eight hours. The fine powder required very little grinding before use. The alcohol treatment is useful in dehydrating the gel partly. It thereby prevents the caking which is generally noticed when water suspensions of alumina are dried. A more adsorbent form of alumina was also prepared by precipitating the gel as described and using the alcoholic suspension without further treatment.

Pure sublimed alizarinic acid was dissolved in absolute alcohol. A saturated solution was found on drying to contain about 1.7 mg / cc. The solutions were allowed to stand in stoppered flasks for three weeks at room temperature in contact with 0.2—0.3 g Al_2O_3. About half the supernatant liquid was removed, centrifuged, and analyzed by the oxidation method described by Weiser.[3] The data are given in Table I and Fig. 1, where No. 1 is with dried alumina, Nos. 2 and 3 with two different samples of suspended alumina. In all three cases the concentrations in the solutions vary continuously and we are therefore dealing with adsorption over the ranges covered by the table.

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* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Coll. Symp. Mon., 7, 161 (1930).

[2] Bull., (3) 25, 862 (1901).

[3] J. Phys. Chem., 31, 1824 (1927).

TABLE I

Alumina and Alizarinic Acid in Alcohol
Length of run: three weeks

A = Milligrams alizarinic acid per gram alumina
B = Milligrams alizarinic acid per cc solution

Dried Alumina				Alumina Suspension			
A_1	B_1	A_1	B_1	A_2	B_2	A_3	B_3
36.5	0.10	76.5	0.85	116	0.00	116	0.08
34	0.18	95	1.07	200	0.07	139	0.36
45	0.25	81	1.18	202	0.33	132	0.72
53	0.31	125	1.43	248	0.50	163	0.77
72	0.52	102.5	1.47	268	0.72	148	1.02

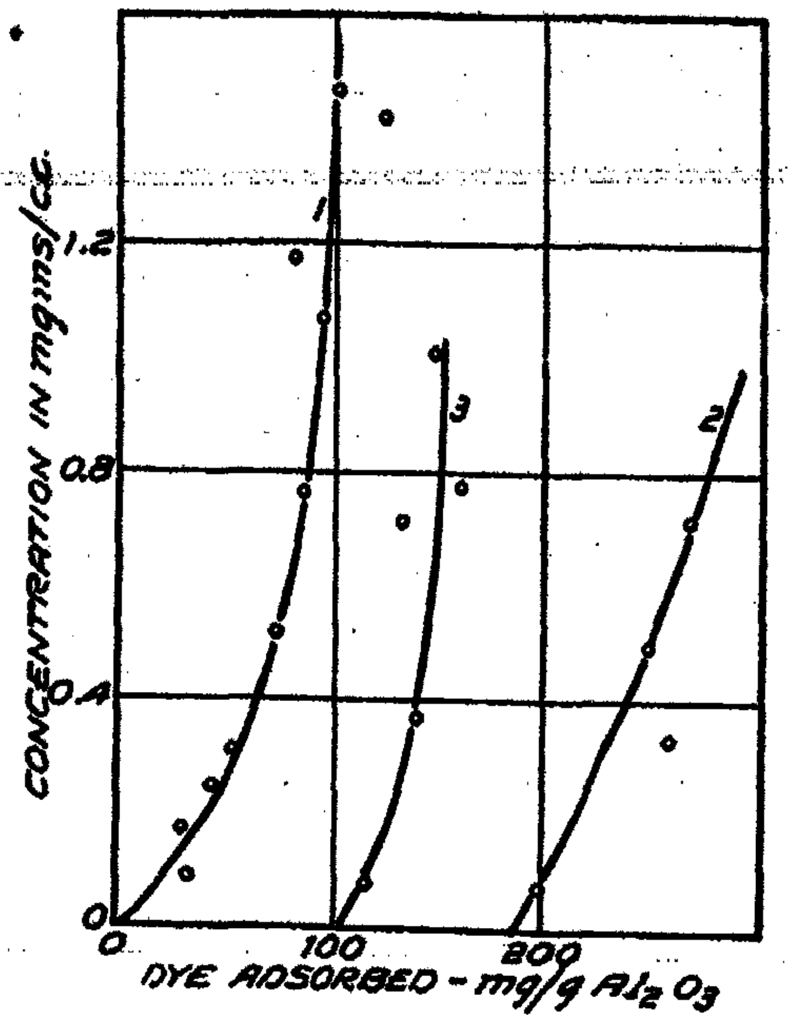

FIG. 1
Alizarinic Acid in Alcohol and Alumina

In Run 2 there is practically complete exhaustion of the bath at low concentrations and it might be claimed that this represented an insoluble compound which then adsorbed alizarinic acid. The simplest answer to this is that 116 mg alizarinic acid per gram alumina corresponds approximately to a formula $Al_{28}(C_{14}H_7O_4)$, which is absurd.

Since Orange II acid is moderately soluble in water, the first run was made with an aqueous solution and a suspension of alumina prepared by precipitating an aluminum chloride solution with ammonia and washing five times by decantation. The concentrations of the stock solutions and the solutions in final equilibrium were determined by the titanous chloride titration method of Knecht,[1] which was found to be quite satisfactory. The data are given in Table II.

TABLE II

Alumina and Orange II Acid in Water
Length of run: three weeks

A = Milligrams Orange II acid per gram alumina
B = Milligrams Orange II acid per cc solution

A	B	A	B
66	0.640	2150	0.625
710	0.640	2890	0.625
1163	0.615	3340	0.615
1808	0.640	3980	0.655

The entire range gives a practically constant value for the concentrations of the solutions, thus showing the existence of two phases and confirming the conclusion of Gordon that a definite chemical compound is formed under these conditions. Qualitative observation of the systems during the progress of the reaction bears out this conclusion. The Orange II lake settles out immediately on mixing and is probably then an adsorption complex. After standing for five days at room temperature needle-like crystals could be observed in all the flasks. Some of these crystals were over an inch long. Careful inspection showed that the powdery mass of almina had been replaced by a mat of crystals. Analyses of some recrystallized samples gave 96.7 percent dye acid instead of 97.3 percent required by AlX_3. That is close enough for our purposes.

One sample of an aqueous alumina suspension, which was about one year old, was treated with an equal volume of the dye acid. Crystals of the aluminum salt were noticed in a few hours. A sample of alumina prepared by heating aluminum nitrate was treated in the same way. This alumina had been shown previously to have practically no adsorbing power for alizarinic acid. With Orange II acid a slight swelling of the particles was noticeable after forty-eight hours. After standing for two weeks the appearance of the sample was very interesting. The large particles of alumina retained their original form; but small radiating crops of needles seemed to sprout from them. At the end of two months the alumina had disappeared partly and a good deal of crystalline material had formed.

When alumina was treated with aqueous solutions of the sodium salt of Orange II, the result was apparently an adsorption isotherm as shown in Table III and Fig. 2.

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[1] Knecht and Hibbert: "New Reduction Methods in Volumetric Analysis" (1925).

TABLE III

Alumina and Sodium Orange II in Water
Length of run: three weeks

A = Milligrams Orange II adsorbed per gram alumina
B = Milligrams Orange II per cc solution

A	B	A	B
411	1.70	1155	5.25
865	3.32	1490	7.02

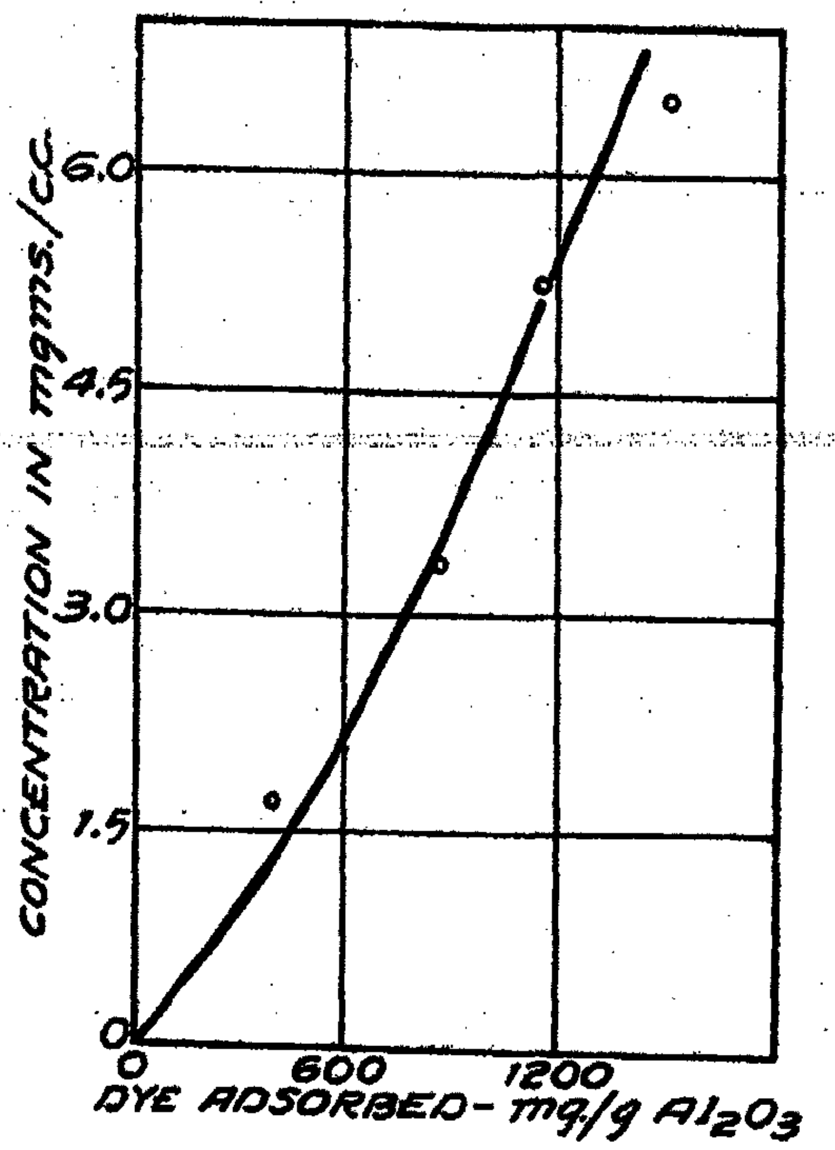

FIG. 2
Sodium Salt of Orange II in Water and Alumina

This unexpected result might be due to one of two causes:

1. Orange II is adsorbed in the form of the sodium salt (the obvious explanation).

2. The dye reacts with alumina to form a definite compound; but the resulting change in caustic soda content is sufficient to cause a variation in the solubility of the compound, which simulates adsorption. The second alternative is ruled out because the pH of the solutions varied between 7.2 and 7.6, whereas, it should have been between 11.0 and 11.8 if all the sodium hydroxide corresponding to the dye had remained in the solution.

On the other hand special analyses showed no decrease in the amount of sodium in the solution. This is analogous to what was found by Weiser for sodium alizarate; the explanation is undoubtedly the same in the two cases.

Our alumina was impure and contained ammonium chloride. The Orange II anions are exchanged for chloride ions and the sodium ions left in solution. If we were to start with a pure alumina, made from amalgamated aluminum, we should undoubtedly get adsorption of the salt of Orange II acid just as was done in the case of sodium alizarate. Unfortunately, time did not permit of this experiment being done at present.

In order to tie in the results with Orange II acid and those with alizarinic acid, a set of experiments was made with alcoholic Orange II acid and an alcoholic suspension of alumina. The results are given in Table IV and Fig. 3.

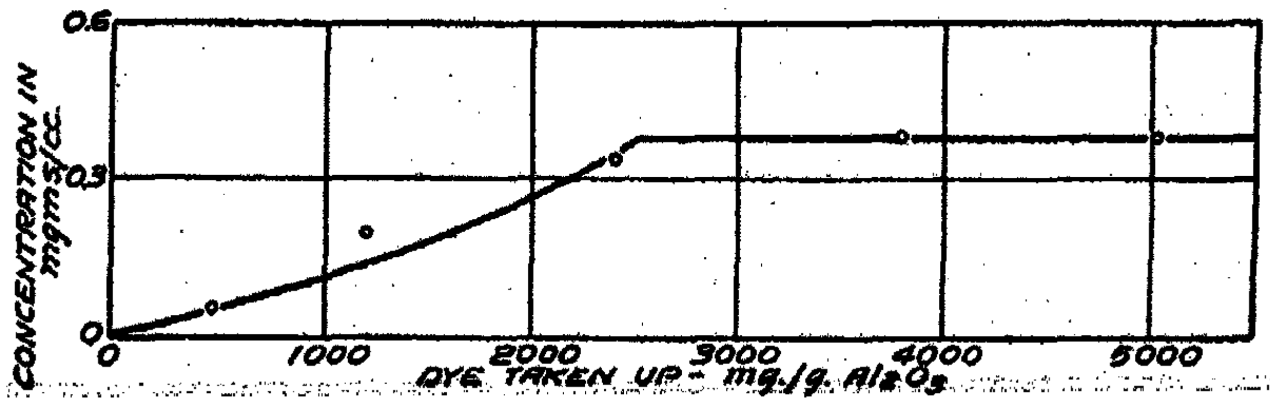

Fig. 3
Orange II Acid in Alcohol and Alumina

TABLE IV

Alumina and Orange II Acid in Alcohol
Length of run: three weeks

A = Milligrams Orange II per gram alumina
B = Milligrams Orange II per cc solution

A	B	A	B
498	0.046	3810	372
1195	0.197	5030	378
2425	0.334		

The curve shows a first portion which seems to indicate adsorption, followed by a flat due to the formation of the chemical compound obtained by Gordon and confirmed by us. It was noticed that crystals of the aluminum salt were plainly visible in the last two reactions flask, while no crystals could be detected in the first three. The alumina, however, was colored orange. Since the aluminum salt of Orange II acid is appreciably soluble in alcohol, the first portion of the curve is of an adsorption curve modified by solubility. For extreme accuracy a correction would have to be made for the amount of aluminum salt in solution. This correction has not been made.

It is not clear why Orange II acid should form a compound readily with alumina while alizarinic acid does not. Orange II is a stronger acid than alizarinic acid; but that is not the whole thing because sulphuric acid, which is a still stronger acid, is adsorbed by alumina from low concentrations in aqueous alcohol.

We hoped to be able to show that alumina precipitated from a sulphate solution would take up less alizarin than alumina precipitated from a chloride solution, because of the greater adsorption of sulphate over chloride. It is well known that some acid dyes which are not affected by sodium chloride can be stripped from wool to some extent by sodium sulphate. This result was not attained because, under the conditions of our experiments, alizarin ions are adsorbed so much more strongly than either sulphate or chloride ions that any difference between the last two is negligible. By adopting a new method of precipitating lakes we were able to get some new and interesting information in regard to alumina-alizarin lakes.

The standard method of making alumina-alizarin lakes is: to precipitate the alumina with ammonia, sodium carbonate, or caustic soda; to wash it several times by decantation or by centrifuging; and then to add the dye to the alumina suspension, usually following this with addition of a solution of calcium acetate to effect more complete precipitation of the dye. Since we wished to study the effect of various salt ions, we substituted for this procedure one which we call the one-step process. This consists in treating a known solution of an aluminum salt with the calculated amount of standard alkali, adding the desired amount of dye immediately. A later improvement by Dr. H. L. Davis is to mix the dye and the alkali, adding this mixture to the solution of the aluminum salt.

The advantages of the one-step method for our purpose are three-fold:

1. It saves the time and loss due to washing.

2. It makes possible the study of the effect of the salts present (NaCl, Na_2SO_4, etc.).

3. It eliminates practically completely effects due to the ageing of the undyed alumina.

It became apparent at once that, in order to use this method to advantage, we needed to know more about the efficiency of alkali and of dye salts in precipitating alumina from solution in the form of a lake. This problem has been discussed in part in the paper,[1] on "Titration Curves for Aluminum Salts with Alkalies." The results which are now given have to do with the effect of sodium alizarate as a precipitating and dispersing agent.[2]

The solutions used were normal aluminum chloride and aluminum sulphate, standard 0.25 N sodium hydroxide and 0.024 N (0.012 M) sodium alizarate. Table V shows a preliminary run with constant equivalent amounts of aluminum chloride and aluminum sulphate, and varying amounts of dye and alkali. The solutions were mixed in the order previously described, the total volume was made up to 20 cc, and observations were made at the end of twenty-four hours. The data are given in Table V.

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[1] Davis and Farnham: J. Phys. Chem., **36**, 1057 (1932).

[2] This property of alizarin has been known for some time. Knecht ("Manual of Dyeing," 2, 574) states that "an excess of alizarin prevents the precipitation of aluminum hydroxide from its salts with ammonia."

TABLE V

Precipitation of Aluminum Salts by Sodium Alizarate and Sodium Hydroxide
One aluminum atom is equivalent to three mols NaOH

Equiv. NaOH	cc dye	Observations
		A 2 cc N $AlCl_3$
2	2	no precipitate formed
3	2	complete precipitation and exhaustion
4	2	partial precipitation; supernatant liquid light orange
2	4	slight precipitation; no exhaustion
3	4	nearly complete precipitation; supernatant liquid slightly yellow
4	4	partial precipitation; exhaustion not complete; supernatant liquid light red
		B 2 cc N $Al_2(SO_4)_3$
2	2	nearly complete precipitation; supernatant liquid light orange
3	2	complete precipitation and exhaustion
4	2	partial precipitation; dark red lake; supernatant liquid light orange
2	4	practically complete precipitation; supernatant liquid light orange
3	4	complete precipitation and exhaustion
4	4	partial precipitation; supernatant liquid light orange

An examination of Table V shows that the precipitation range for the sulphate lakes is wider than that for the chloride lakes, which is in accord with what had been found previously for the action of alkali alone upon aluminum salts. Sodium alizarate behaves in general something like sodium hydroxide, causing precipitation in small amounts and dispersion in large amounts.

In Table VI are given results when the aluminum chloride or sulphate was kept constant at 2 cc, and the caustic soda at two equivalents, while the amount of dye varied. In order to simplify the tabulation, the following symbols are used for describing the tubes:

1. Indicates a clear solution; red with no precipitate.
2. Indicates partial precipitation of alumina.
    a) complete exhaustion.
    b) incomplete exhaustion.

    (degree of exhaustion is indicated by minus signs for very slight color in the supernatant liquid and by plus signs for much color).
3. Indicates complete precipitation of alumina.
    a) complete exhaustion.
    b) incomplete exhaustion.

It is somewhat difficult to judge between 2 and 3. The variation in the volume of the precipitate was used as a preliminary indication and confirmed by testing the liquid with ammonia.

TABLE VI

Precipitation and Peptization of Alumina Lakes by Varying Concentrations of Sodium Alizarate

A = 2 cc N $AlCl_3$; B = 2 cc N $Al_2(SO_4)_3$
Equivalents of sodium hydroxide = 2
O = observations after twenty-four hours

cc dye	O-A	O-B	cc dye	O-A	O-B
1	2b	2a	7	1	1
2	3a	3a	8	1	1
3	2b	2b +	9	1	1
4	1	1	10	1	1
5	1	1	11	1	1
6	1	1	12	1	1

At the end of twenty-four hours all those tubes which did not give clear, colorless, supernatant solutions (those not marked 2a or 3a) were treated as follows:

Five cc of the supernatant liquid were drawn off and placed in a small test-tube. To the aluminum chloride solutions there were added 5 cc of saturated sodium chloride solution, while an equivalent amount of saturated sodium sulphate solution was added to the aluminum sulphate solutions. The tubes were stoppered, shaken, and examined after having stood for twenty-four hours. This use of two different salt solutions is not the usual procedure. In these experiments the object was to have the two systems exactly comparable except for one variable, the inorganic anion. By using the same anion in the aluminum salt and in the added salt it is possible to observe the difference due to only one cause with no complicating factors to consider, such as would result if we used chloride and sulphate initially and sulphate finally in both cases. This would give in one case three competing anions, sulphate, hydroxyl, and alizarate; in the other case four, sulphate, hydroxyl, alizarate, and chloride. The results are given in Table VII.

TABLE VII

Flocculation of Peptized Alumina-Alizarin Lakes

A = aluminum chloride lakes with sodium chloride
B = aluminum sulphate lakes with sodium sulphate
O = observations after twenty-four hours
cc dye = concentration of dye per 20 cc in original

cc dye	O-A	O-B	cc dye	O-A	O-B
1	3a	—	7	*	1
2	—	—	8	*	1
3	3a	3a	9	*	1
4	3a	3a	10	3b	3b
5	3a	$3b^{---}$	11	3b	$2b^{+}$
6	$3b^{---}$	$3b^{---}$	12	2b(?)	$2b^{++}$

* These tubes show the full red color; but a partial precipitation of the lake can be detected by a cloudiness at the bottom of the tubes.

All tubes containing more than 3 cc dye fail to form precipitated lakes. This is due to the fact that the dye anions, being adsorbed strongly, exert a peptizing action upon the lake which is comparable with that of excess sodium hydroxide. For alumina alone about 4.2 equivalents of alkali are sufficient to redisperse alumina in an aluminum chloride system, while 4.7 equivalents is needed for the sulphate system. If we consider 4 cc of dyes being the first completely redispersed system in the presence of two equivalents of caustic soda, we must then assume that 4 cc of the dye are equivalent to at least 2.2 NaOH. Since the dye solution is 0.024 normal, 4 cc = 0.0096 normal cc. 2 equivalents of NaOH = 1.33 normal cc per 2 cc $AlCl_3$, 4.2 equivalents of NaOH = 1.4 cc and 1.33 + 0.096 = 1.429 cc. It is thus evident that the dye solution is about equivalent in peptizing power to the same amount of sodium hydroxide. This knowledge is very useful in the preparation of alizarin lakes by the one-step process.

In the chloride suspensions of alumina a positively charged lake is formed in the presence of 1 cc of dye. This is due to the fact that an excess of aluminum chloride is present, the peptizing power of the strongly adsorbed, trivalent aluminum ion overcoming the effect of the weakly adsorbed chlorine ions and stabilizing the sol. In the sulphate solutions the bivalent sulphate ions are adsorbed strongly enough on the acid side to prevent this action.

The addition of sodium chloride or sodium sulphate flocculates the sols resulting from the presence of an excess of dye, even though these are negatively charged sols. The flocculation must be due to an adsorption of sodium ions in preference to chlorine and sulphate ions. With the negatively charged sols there is thus a reversal of the anion effect, sodium sulphate having less flocculating power than sodium chloride because sulphate ion is adsorbed more strongly than chloride ion and therefore tends to keep the sol more negative. This is identical with what was observed years ago with albumin sols. Both alumina sols show a region of maximum stability on addition of a definite amount of sodium chloride or sulphate. For this concentration this region occurs with 7-9 cc dye. The sulphate sols remain perfectly clear for twenty-four hours after the addition of salt, while the chlorides are precipitated partially. Beyond this range is another of comparatively low stability, followed by a third, stable, repeptization zone. This is a striking example of the well-known irregular series.[1]

It is easy to see that the action of alkali on aluminum sulphate and aluminum chloride should produce a precipitate at lower concentrations in the sulphate solutions; but it is not at all clear why more alkali is necessary to peptize the alumina from the sulphate solution. It should be the other way round. This probable explanation is that the difference is apparent and not real, being due to the fact that the alumina from the sulphate solution is much denser and is apparently less hydrous than that from the chloride solution.

Bancroft and Ackerman[2] have accounted for the polygenetic nature of alizarin with different mordants by postulating the presence of yellow, un-

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[1] Kruyt and van Klooster: "Colloids" (1927).

[2] J. Phys. Chem., 35, 2568 (1931).

dissociated alizarinic acid, red alizarate ion, and purple undissociated sodium alizarate. Dr. H. L. Davis has pointed out to us that it would be more in line with the views of Hantzsch[1] to postulate the existence of several, colored, tautomeric, alizarinic acids. Sörensen[2] describes the use of alizarin as an indicator. He records two distinct color changes: yellow to red at pH 5-5-6.8, and violet to purple at pH 10.1-12.1; the change from red to violet is gradual. By very careful addition of alkali to a dilute solution of alizarinic acid, one easily obtains all four colors: yellow, red, violet and purple (blue). Even assuming that the violet form is a mixture of red and the blue, there are three, distinct, colored forms of alizarinic acid, and it is necessary to assume some tautomeric changes to account for these differences.

The nature of the solvent often has a great effect on the equilibrium between two forms, but it should have no effect on the nature of the form crystallizing from the solution, provided the crystals do not contain solvent of crystallization. Meyer and Jacobson,[3] not knowing the phase rule, state that alizarinic acid crystallizes in yellow crystals from alcohol, but in orange-red crystals from other organic solvents. Special experiments showed that solutions of alizarinic acid in chloroform, carbon tetrachloride, ether, n-butyl bromide, and paraldehyde are yellow, solutions in alcohol and acetone are orange-yellow, and solutions in benzaldehyde are orange. Alizarin crystallized from these solvents in yellow to yellow-orange crystals, depending on the size of the crystals. When powdered, all the crystals were the same yellow.

The behavior of a pyridine solution is interesting. In pure, dry pyridine alizarin dissolves to form a yellow solution. On dilution with a small amount of water the solution becomes red, changing to purple as still more water is added. This change is in the direction one would expect from increasing alkalinity.

If the polygenetic character of alizarin is due to tautomerism and if this tautomerism is affected by the pH of the solution, it should be possible to change the color of alizarin lakes by varying the pH. Experiments were therefore made with alumina and tin lakes.

It was found possible by special manipulations to change the color of the alumina-alizarin lake through the entire series from yellow to violet and back to red. The alumina was prepared by heating aluminum nitrate. While this alumina does not take up much alizarin, it has the advantage of not being peptized readily by acid or alkali. A dilute solution of alizarinic acid in alcohol was treated with a slight excess of caustic soda. While sodium alizarate is not very soluble in alcohol, a purple, apparently clear, solution can be obtained. When shaken with alumina a lavender lake was obtained, which changed to pink on washing with water. Washing with a three percent tartaric acid solution changed the color to yellow. Washing with caustic soda solution restored the original lavender color. A red lake was prepared by treating alumina with alcoholic alizarinic acid. When treated with a solution of phosphoric acid, the lake became yellow. Washing with caustic soda solution changed the lake to a violet red.

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[1] Cf. Heinrich (Johnson and Hahn): "Theories of Organic Chemistry," 382-478 (1922).

[2] Biochem. J., **21**, 241 (1909).

[3] "Lehrbuch der organischen Chemie," 2, II, 555 (1903).

Tin mordant was prepared by the method described by Ackerman. It was suspended in alcohol and treated with an alcoholic solution of alizarinic acid. A yellow lake was formed. The mixture was made alkaline with ammonia, after which acetic acid was added drop by drop until a red shade resulted. On filtering, a red lake was formed which was fairly deep in color and reasonably fast to washing with alcohol and water. The color is actually more nearly an orange red than the cherry red of the alumina lakes. With sodium alizarate and alkali tin gives a purple lake.

We see that alumina lakes are red over a wide range of pH; but can be obtained yellow or purple. With stannic oxide the red lake exists only over a narrow range of pH, the yellow occurring over most of the acid range and the purple over most of the alkali range. With other mordants one would probably get ranges intermediate between these two extremes.

The general results of this investigation are:

1. By using alcohol as a solvent it is possible to make a phase rule study of alizarinic acid and alumina.
2. Kahlbaum's alumina is practically inert towards alizarin. Alumina obtained by heating aluminum nitrate adsorbs alizarin slightly. A precipitated alumina dried at 100° is a moderately good adsorbent. Freshly precipitated, washed alumina is a good adsorbent.
3. At ordinary temperatures alizarin forms no definite chemical compound with alumina. The alumina-alizarin lakes are adsorption complexes. This confirms the results of Weiser and Porter.
4. Orange II acid forms a definite chemical compound, AlX_3, with alumina both in aqueous and in alcoholic solution. This confirms the results of Reinmuth and Gordon. At low concentrations Orange II acid is adsorbed by alumina. This was not discovered by Reinmuth and Gordon, who did not study this range.
5. The sodium salt of Orange II is adsorbed by alumina, no definite chemical compound being formed. This was not discovered by Reinmuth and Gordon.
6. Caustic soda and sodium alizarate have been shown to be nearly equivalent in the precipitation and dispersion of alumina.
7. The negatively charged lakes formed by peptization with sodium alizarate are destabilized by sodium chloride and sodium sulphate owing to adsorption of sodium ions. There is a reversal of the order of the anions just as there is with albumin.
8. The color of an alizarin solution can be varied over the entire range from yellow to red to violet (to blue) by a progressive increase in pH. Since this is apparently due to tautomeric changes, one must at least assume the existence of yellow, red, and blue (purple) alizarinic acids.
9. The colors of alizarinic acid dissolved in pyridine can be varied through the entire range by adding water which increases the alkalinity.
10. Under suitable conditions one can prepare alumina and tin lakes of all the colors. With alumina the red is stable over a wide range of pH and with tin over a narrow range.

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ELECTROKINETICS XII. INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS II. Al_2O_3—ORGANIC LIQUID INTERFACES*

BY OTTO G. JENSEN AND ROSS AIKEN GORTNER

Introduction

Considering the ultimate electrical nature of matter, it is logical to expect that measurements of the electrical properties of a molecule would prove fruitful in elucidating its structure. This has proved to be the case. Determinations of the dielectric constants of organic compounds have been numerous. In themselves, they are of limited value, but together with density and refractive index determinations, they play an important part in the newer theories of the structure of matter. The dipole moment of a molecule is a measure of its electrical asymmetry. Phenomena such as molecular association and adsorption are caused by the stray electric fields of molecules resulting from a lack of balance amongst their electrical components.

This study is concerned with the measuring of these unbalanced electrical forces at the boundary of two contiguous phases. More specifically, it is a study of the molecular structure of certain organic compounds by means of streaming potential technic.

Historical

The literature has been already adequately reviewed by Briggs,[1] Bull and Gortner,[2] and Martin and Gortner[3] in earlier papers in this series, so that only the more recent contributions need mention.

Most of the records in the literature are expressed in terms of the electrokinetic potential (ζ-potential) calculated by the formula

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon} \qquad (1)$$

where η = coefficient of viscosity, H = observed E.M.F., κ_s = specific conductance of the liquid in the diaphragm, P = hydrostatic pressure, ϵ = dielectric constant.

Bull and Gortner[2,4] have determined the effect of different electrolytes in various concentrations on the ζ-potential, the density of charge, and the

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* Published as Paper No. 1112. Journal Series, Minnesota Agricultural Experiment Station. Condensed from a thesis presented by Otto Gerhard Jensen to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1931.

[1] J. Phys. Chem., 32, 641:675 (1928).

[2] J. Phys. Chem., 35, 309-330 (1931).

[3] J. Phys. Chem., 34, 1509-1539 (1930).

[4] J. Phys. Chem., 35, 700-721 (1931).

thickness of the double layer. They found that, in general, the ζ-potential decreased with increasing concentration, but that the charge per unit area of surface increased. They point out that, at least for univalent ions, the discharging of colloidal particles may be due more to a decrease in the thickness of the double layer than to an actual diminishing of the charge. They were unable to detect any antagonistic action between NaCl and KCl, NaCl and $CaCl_2$, or $CaCl_2$ and $MgCl_2$. They point out that the calculated ζ involves a knowledge of the dielectric constant, which in the adsorbed film is probably different from the bulk value. They accordingly propose[6] that, instead of ζ, electrokinetic measurements be expressed in terms of qd, the *electric moment per unit area,* which can be calculated using only the experimentally determined values by the formula

$$\mathrm{qd} = \frac{\eta\kappa_s \mathrm{H}}{\mathrm{P}} \qquad (2)$$

where q is the charge per unit area of the double layer and d is its thickness, the other quantities being the same as in equation (1), all expressed in electrostatic units.

Determinations of the electrokinetic potentials at solid-organic liquid interfaces have not been numerous. Quincke[7] was the first one to study the electro-endosmose of organic liquids. He found that turpentine was negatively charged in respect to asbestos, clay, quartz, shellac, and silk, whereas water was positively charged. The work of Strickler and Mathews[8] shows that Coehn's[9] rule does not hold for the organic solvents which they studied, but that the dielectric constant ratio does affect the magnitude of flow. They made no attempt to correlate their findings with the structure of the compounds.

Martin and Gortner[3] have obtained striking correlations between the electrokinetic potentials at cellulose-organic liquid interfaces, as obtained by streaming potential measurements, and the molecular structure of the organic compounds. For a homologous series of normal aliphatic alcohols, the introduction of a $-CH_2$ group into the chain changes the ζ-potential approximately ±36 millivolts. The substitution of a methyl group for a hydrogen atom to form a branched-chain alcohol alters the ζ-potential to the extent of only ±4 millivolts. Benzene gave no streaming potential. In the case of substitution for a hydrogen atom in the benzene molecule, the groups affected the ζ-potential in the following order: $CH_3 < Cl < Br < NH_2 < NO_2$.

Fairbrother and Balkin[10] have made a careful study of the electro-endosmose of 14 pure organic liquids through a diaphragm of sintered Jena Geräte glass powder. They conclude that there is a very close relationship between the electro-endosmotic velocity of an organic compound and its dipole moment.

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[6] Bull and Gortner: Physics, 2, 21-32 (1932).

[7] Pogg. Ann., 113, 513-598 (1861).

[8] J. Am. Chem. Soc., 44, 1647-1662 (1922).

[9] Wied. Ann., 64, 217-232 (1898).

[10] J. Chem. Soc., 389-403 (1931).

Experimental

The problem.—In the light of the findings of Martin and Gortner,[3] it was thought that a further investigation into the relationship between molecular configuration and interfacial energy might prove fruitful. The present report deals with such a study using (1) an homologous series of 5 normal aliphatic acids, (2) an homologous series of the normal aliphatic alcohol-esters of acetic acid and (3) a series of the ethyl esters of certain of the normal aliphatic acids, against aluminum oxide.

The chemicals used may be expressed as (1) R—COOH, (2) CH_3—CO—O—R and (3) R—CO—O—C_2H_5 where R stands for a series of straight chain aliphatic radicals differing from each other by —CH_2—. If the electrokinetic effect at the interface is produced by the unbalanced polarity of the molecules oriented at the interface, as suggested by Martin and Gortner,[3] then it should be interesting to observe the relative effect on such a measurement when a given radical is attached (1) directly to the carbon of a carbonyl group or (2) when it is separated from the carbonyl group by the oxygen of an ester linkage.

The method.—Streaming potential apparatus essentially identical with that used by Martin and Gortner[3] was used. Since this has been adequately described by them, the description will not be repeated. Two modifications of the apparatus were found necessary.

Because of the high voltages which were produced by the streaming liquid, it became necessary to insert four 6-volt lead-acid storage batteries (automobile type) and three units of 48-volt lead-acid storage batteries (radio B-battery type), connected in series, to be used as a potential source to be balanced through the potentiometer against the E.M.F. generated by the streaming liquid, using the quadrant electrometer as a null instrument. It was thus possible to accurately measure streaming potential E.M.F.'s as great as 150 volts.

The second modification dealt with the method for measuring the specific conductivity of the liquids in the pores of the diaphragm. It was discovered that the resistances of most of the liquids in the diaphragm were too large to be measured with the ordinary Wheatstone bridge using either a 1000-cycle current and telephones or a 60-cycle current and an alternating current galvanometer of 0.025 microampere sensitivity. Accordingly, the apparatus was so designed that the resistance measurements could be made by a direct current method, employing the electrometer as the null-point instrument. Potentials of approximately 150 volts were applied to the bridge arm containing the cell to balance the current furnished by the potentiometer and passing through a standard megohm resistance.

The arrangement of apparatus for measuring the resistance of the diaphragm containing the organic liquid is given in Fig. 1. Zero deflection of the electrometer *E* is obtained by balancing the current through the diaphragm *D* under the potential of *B*, against the current through the standard megohm resistance *R* under the potential at *A*. *B* is a 150-volt storage battery, and the potential at A is led off from a L. and N. type K potentiometer. The ratio of the potentials required, B/A, is equal to the resistance of D in megohms, the resistance of A and B being neglected. Reversing the polarities, repeating the determination, and averaging the results, obviates any error arising from a potential produced in the cell caused by a difference in the levels of the liquid.

For the determination of the cell constant, the liquid is removed and the diaphragm washed three times with ethyl alcohol and three times with portions of the 0.1 N KCl solution to be used for the determination. The cell is now introduced into one arm of a Wheatstone bridge and the determination completed in the usual manner, using a 60-cycle current and an alternating current galvanometer as a null-point instrument.

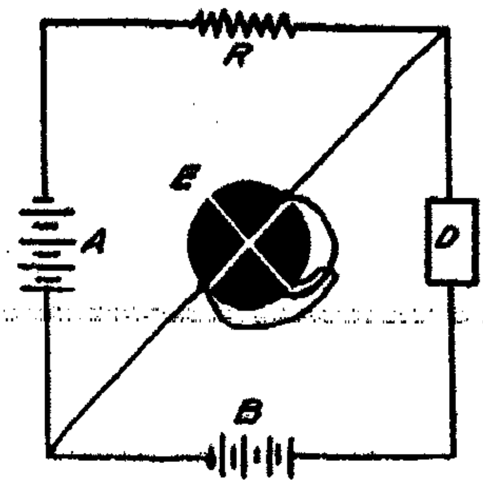

Fig. 1

Diagrammatic arrangement of the bridge for the measurements of high resistivity.

Aluminum oxide* which had been exhaustively extracted through a period of several months with many liters of distilled water, during the whole of which time it was in contact with a large volume of water, was used as the diaphragm material. Prior to use, it had been dried at 110° for 72 hours.

Twenty-four hours before the determination was to be made, sufficient aluminum oxide to fill the glass cell was suspended in the liquid to be studied. The aluminum oxide was then packed into the cell by tamping with a glass rod.

Two perforated gold electrodes were placed at each end of the diaphragm, and between the double electrodes there was inserted a disk of fine cloth (batiste) to prevent the aluminum oxide sifting through the perforations. No error was introduced by this procedure, for the leads from the two electrodes on the same side of the diaphragm were "shorted" by being placed into the same mercury cup. Cork gaskets were employed between the electrodes and between the electrodes and the glass parts. The cell was then filled with the liquid to be studied, placed in the constant temperature bath, and connected to the pressure line.

After a lapse of one-half hour to allow the cell to assume the temperature of the bath, streaming potentials were determined. All of the determinations were made at 30°C.

Calculation of Results.

(A) *Constants Employed.* In Table I are given the values for ϵ the dielectic constant, η the coefficient of viscosity, and μ the dipole-moment used in calculating the values presented in Tables II to XVII.

The values for ϵ and η have been taken from the Critical Tables with the exception of those values for η which bear an asterisk. These were determined by means of an Ostwald type viscometer. The values for μ are those compiled by Smyth.[11]

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* Our thanks are due Dr. Francis Frary of the Aluminum Company of America for providing us with a large sample of aluminum oxide.

[11] "Dielectric constant and molecular structure" (1931).

TABLE I

Liquid	ϵ	η	$\mu(\times 10^{18})$
Acetic acid	6.2	0.0104	1.4
Methyl acetate	6.7	0.00344	1.75
Ethyl acetate	6.25	0.00401	1.80
n-Propyl acetate	6.2	0.00513	1.86
n-Butyl acetate	5.0	0.00658*	1.85
n-Amyl acetate	4.95	0.00757*	1.91
Ethyl formate	7.0	0.00375	1.93
Ethyl n-propionate	5.7	0.00473	1.79
Ethyl n-butyrate	5.1	0.00604	—
n-Propionic acid	3.2	0.00963	1.74
n-Butyric acid	2.8	0.0134	0.9
n-Valeric acid	2.6	0.0186	—
n-Caproic acid	3.2	0.0256	—

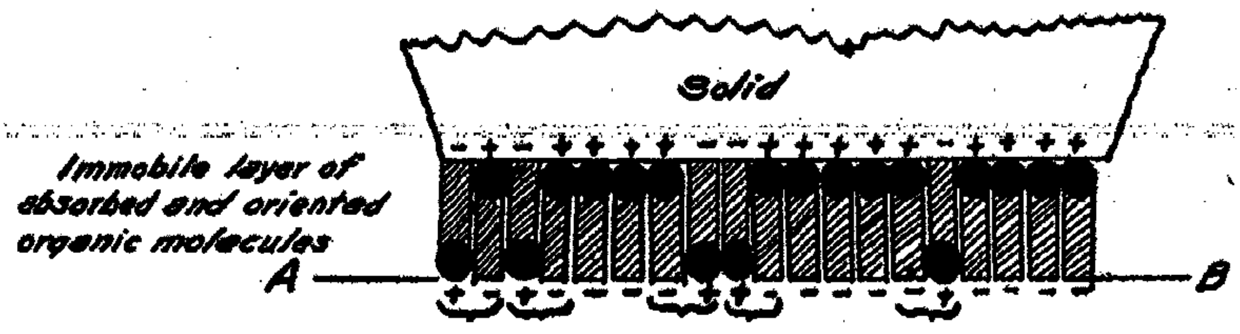

FIG. 2

A diagrammatic representation of the oriented adsorption of organic dipoles at a solid liquid interface. Postulated as a source of the electric double layer.

(B) *Calculation of Electrokinetic Potential* (ζ). The zeta potential is calculated from the formula, $\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon}$. To express ζ in millivolts, $\zeta = 847{,}649 \frac{\eta H\kappa_s}{P\epsilon} \times 10^6$, where η = coefficient of viscosity, H = streaming potential in volts, κ_s = specific conductivity of the liquid in the diaphragm in reciprocal ohms, P = pressure in centimeters of mercury, ϵ = dielectric constant of the liquid.

(C) *Calculation of Electric Moment of the Double Layer* (qd). The electric moment for a unit area of the double layer is calculated from the formula, $qd = \eta H\kappa_s/P$. To express qd in electrostatic units, $qd = 226{,}200\,\eta H\kappa_s/P$, where η, H, κ_s and P have the same meaning as above.

(D) *Unbalanced Orientation of the Molecules in the Interface.* Martin and Gortner[3] have suggested that the electrokinetic potential at a solid-organic liquid interface arises from an oriented adsorption of organic molecules. If organic dipoles are oriented at an interface, we might expect an arrangement more or less like that shown diagrammatically in Fig. 2. Assuming a plane of sheer at A-B, the bracketed pairs of dipoles, oriented in opposite directions, might be expected to neutralize each other, whereas the "unbalanced orientation" of the remaining molecules should give rise to a net negative charge on the "immovable layer" side of the interface with a corresponding positive charge in the steaming liquid.

On this hypothesis, it should be possible to calculate the percentage of "unbalanced orientation" of the organic molecules in the immovable layer assuming (1) a monomolecular, close-packed, oriented layer, and (2) that the electric moment per unit area of the double layer is the product of the dipole moment of the organic molecule and the number of "unbalanced" molecules oriented per unit area.

In our calculations, the values for the cross-sectional area of the molecules (A) are those given by Rideal[12] for the limiting areas per molecule in the liquid condensed form. For esters A = 22.0 Å^2 and for acids A = 24.4 Å^2.

The per cent of the total surface occupied by oriented but "unbalanced" molecules is given by the expression, $qd\ A/\mu 10^{14}$, where μ is the dipole moment, and qd and A have the meaning denoted above.

Presentation of Data

The streaming potentials at various pressures for the fifteen liquids studied are presented in Tables II to XVI. In the formula, $\zeta = 4\pi\eta H\kappa_s/P\epsilon$, it is assumed that H/P is a constant. The validity of this assumption is demonstrated by the values in the third column of each table. Included is the specific conductivity of the liquid in the diaphragm (κ_s) and the calculated values for the zeta potential, the electric moment of the double layer, and the percent of the "unbalanced" oriented molecules in the interface. The sign of the charge on the aluminum oxide phase is given parenthetically. Table XVII summarizes these values. They are shown graphically in Fig. 3 and 4.

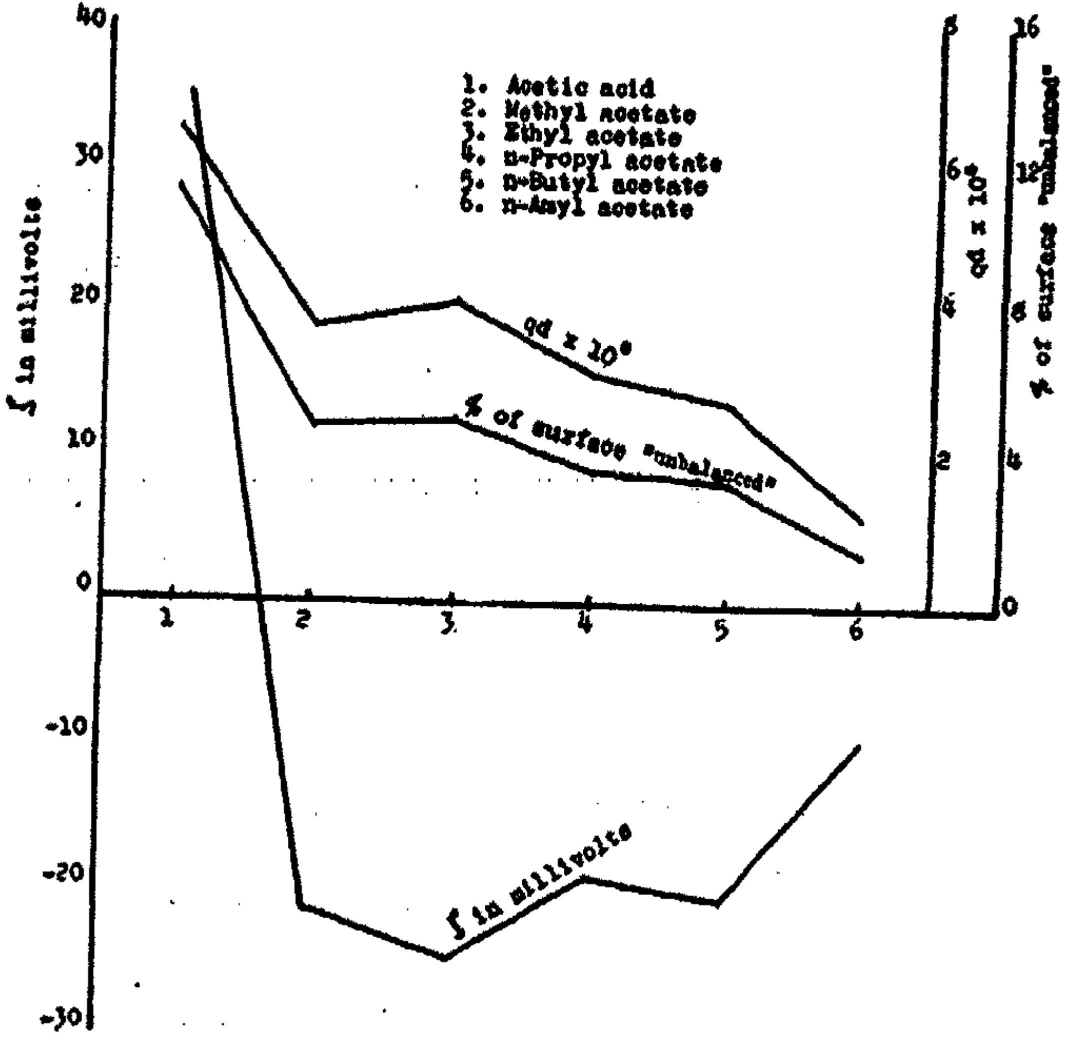

Fig. 3

The electrokinetic potentials, the electric moment per unit area, and the precent of "unbalanced" oriented molecules at an Al_2O_3—organic liquid interface for a series of the n-aliphatic esters of acetic acid.

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[12] "Surface Chemistry," 100 (1930).

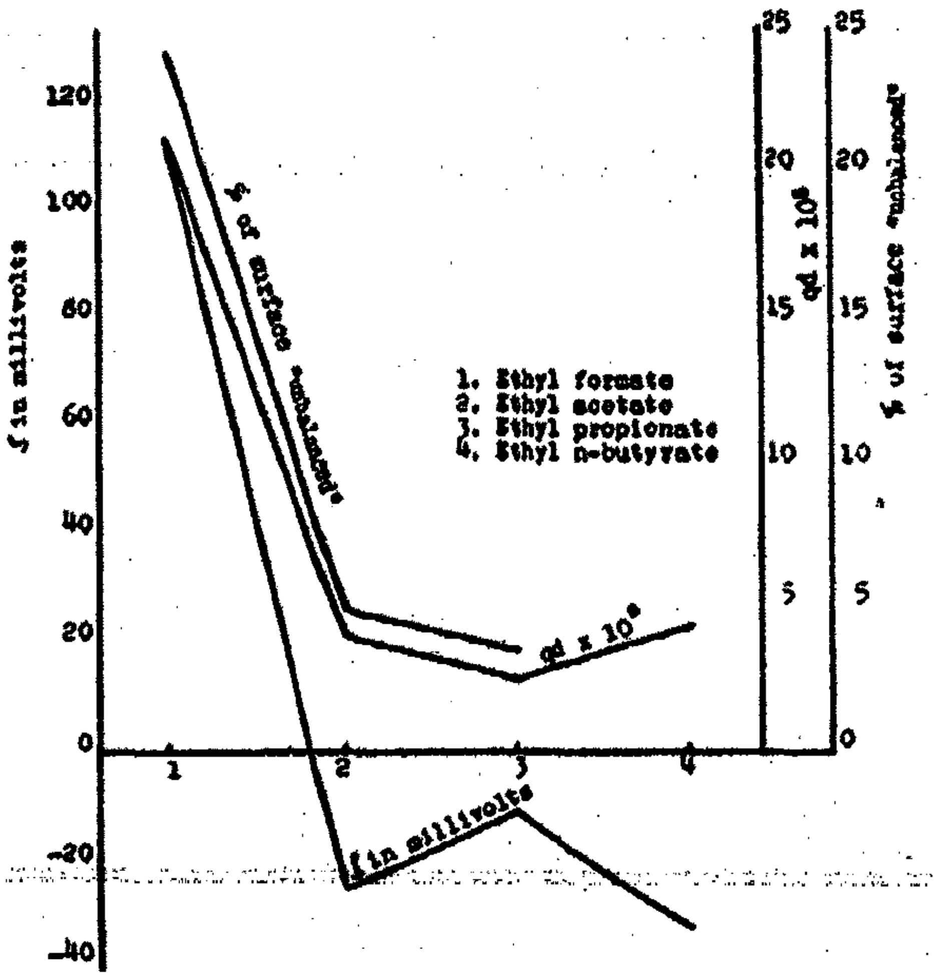

FIG. 4

Data similar to that shown in Fig. 3 for an Al_2O_3—organic liquid interface for a series of the ethyl-esters of certain of the n-aliphatic acids.

TABLE II

Data for Acetic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v)}}{P \text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v)}}{P \text{ (cm Hg)}}$
65.4	0.6826	0.104	101.0	1.2511	0.124
77.0	0.8839	0.115	111.0	1.2881	0.116
84.3	0.9720	0.115	160.5	1.9790	0.123
92.5	1.0812	0.117		Average =	0.116

$\kappa_s = 2.39 \times 10^{-7}$, $\zeta = 39.4$ m.v., qd $= 6.52 \times 10^{-5}$, "Unbalanced" oriented molecules = 11.4%.

TABLE III

Data for Methyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P \text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P \text{ (cm Hg)}}$
255.0	66.020	2.59	68.8	18.670	2.71
227.3	57.625	2.54	52.5	14.000	2.67
173.7	45.655	2.63	35.1	9.668	2.75
131.7	35.090	2.66	19.8	5.596	2.83
99.5	26.870	2.70		Average =	2.68

$\kappa_s = 1.86 \times 10^{-8}$, $\zeta = 21.7$ m.v., $qd = 3.88 \times 10^{-5}$, "unbalanced" oriented molecules = 4.88%.

TABLE IV

Data for Ethyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$
13.3	21.235	15.97	49.8	79.69	16.00
18.0	29.00	16.11	63.8	102.70	16.10
27.0	43.42	16.08	73.6	118.30	16.07
38.8	62.21	16.03		Average =	16.06

$\kappa_s = 2.84 \times 10^{-9}$, $\zeta = 24.8$ m.v., $qd = 4.14 \times 10^{-5}$, "unbalanced" oriented molecules = 5.05%.

TABLE V

Data for n-Propyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$
15.6	22.605	14.49	50.5	72.590	14.37
21.0	30.235	14.40	60.2	90.140	14.97
25.6	36.750	14.36	66.1	97.970	14.82
32.3	45.940	14.22	71.8	108.920	15.17
40.6	59.750	14.71	76.7	114.300	14.90
				Average =	14.64

$\kappa_s = 1.87 \times 10^{-9}$, $\zeta = 19.2$ m.v., $qd = 3.17 \times 10^{-5}$, "unbalanced" oriented molecules = 3.75%.

TABLE VI

Data for n-Butyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$
18.4	53.14	28.88	29.7	90.00	30.30
19.5	57.64	29.57	31.5	93.96	29.83
20.8	60.70	29.18	34.3	102.29	29.82
23.3	70.00	30.04	38.4	114.95	29.93
24.7	72.57	29.38		Average =	29.66

$\kappa_s = 6.23 \times 10^{-10}$, $\zeta = 20.6$ m.v., $qd = 2.75 \times 10^{-5}$, "unbalanced" oriented molecules = 3.27%.

TABLE VII

Data for n-Amyl Acetate—Aluminum Oxide (−) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F. (v.)}}{P\text{ (cm Hg)}}$
25.1	8.28	3.30*	108.0	72.50	6.71
62.9	41.65	6.62	121.5	84.70	6.97
50.4	36.41	7.22	141.3	104.03	7.36
83.7	59.37	7.09		Average =	7.00

* Omitted in calculation of average.

$\kappa_s = 1.05 \times 10^{-9}$, $\zeta = 9.53$ m.v., $qd = 1.26 \times 10^{-5}$, "unbalanced" oriented molecules = 1.45%.

TABLE VIII

Data for Ethyl Formate—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$
33.0	.1024	.0310	120.6	.3582	.0297
48.4	.1440	.0292	156.0	.4705	.0302
65.2	.1880	.0288	207.0	.6295	.0304
74.3	.2150	.0289	246.5	.7500	.0304
94.4	.2670	.0283	303.0	.9221	.0304
				Average =	.0297

$\kappa_s = 8.41 \times 10^{-8}$, $\zeta = 113$ m.v., $qd = 21.2 \times 10^{-5}$, "unbalanced" oriented molecules = 24.1%.

TABLE IX

Data for Ethyl Propionate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$
36.8	46.05	12.51	64.2	80.10	12.47
41.2	51.53	12.51	72.4	90.97	12.56
48.6	61.95	12.75	78.9	98.25	12.45
55.0	68.32	12.42		Average =	12.52

$\kappa_s = 2.17 \times 10^{-9}$, $\zeta = 10.8$ m.v., $qd = 2.90 \times 10^{-5}$, "unbalanced" oriented molecules = 3.56%.

TABLE X

Data for Ethyl n-Butyrate—Aluminum Oxide (–) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$
42.2	30.66	7.26	69.0	50.80	7.36
53.5	41.75	7.80	77.4	54.45	7.03
60.4	46.09	7.63		Average =	7.42

$\kappa_s = 4.30 \times 10^{-9}$, $\zeta = 32.1$ m.v., $qd = 4.36 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value of μ is lacking.

TABLE XI

Data for Propionic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P\text{ (cm Hg)}}$
21.5	30.13	14.01	48.2	61.63	12.79
31.8	44.45	13.98	55.5	71.11	12.81
36.9	46.65	12.64	72.2	80.63	11.17
42.0	54.50	12.98	86.6	95.76	11.06
				Average =	12.68

$\kappa_s = 5.77 \times 10^{-10}$, $\zeta = 18.66$ m.v., $qd = 1.67 \times 10^{-5}$, "unbalanced" oriented molecules = 2.34%.

TABLE XII

Data for n-Butyric Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$
30.0	34.93	11.64	66.6	67.82	10.18
39.3	42.56	10.83	75.8	77.38	10.21
48.6	51.49	10.59	86.3	86.00	9.97
54.7	56.01	10.24		Average =	10.52

$\kappa_s = 4.07 \times 10^{-9}$, $\zeta = 173.7$ m.v., * $qd = 13.0 \times 10^{-5}$, "unbalanced" oriented molecules = 35.2%.

* See footnote to Table XVII.

TABLE XIII

Data for n-Valeric Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$
30.2	13.60	4.50	73.4	38.51	5.25
33.6	14.37	4.28	84.8	44.94	5.21
36.2	14.55	4.02	98.2	54.16	5.52
56.2	27.58	4.85	107.7	61.35	5.69
				Average =	4.92

$\kappa_s = 4.06 \times 10^{-10}$, $\zeta = 12.1$ m.v., $qd = 0.84 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value of μ is lacking.

TABLE XIV

Data for n-Caproic Acid—Aluminum Oxide (+) Interface

Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$	Pressure in mm Hg	E.M.F. in volts	$\frac{\text{E.M.F.(v.)}}{P \text{ (cm Hg)}}$
29.9	47.08	15.75	67.7	101.75	15.03
40.0	61.46	15.37	73.7	106.02	14.39
52.7	82.54	15.66	78.7	111.41	14.16
58.2	88.59	15.22	94.0	128.13	13.63
				Average =	14.90

$\kappa_s = 2.87 \times 10^{-10}$, $\zeta = 29.0$ m.v., $qd = 2.48 \times 10^{-5}$, % of "unbalanced" oriented molecules can not be calculated because value for μ is lacking.

TABLE XV

Data for Benzene—Aluminum Oxide Interface

Pressure in mm Hg	E.M.F. in volts
35.3	0
66.0	0

There is a small erratic potential, + or −, at times, but for the greater part of the time there is no E.M.F. It is concluded that impurities cause the spurious potentials and that the zeta potential for a benzene-aluminum oxide interface is zero.

TABLE XVI

Data for Carbon Tetrachloride—Aluminum Oxide Interface

Pressure in mm Hg	E.M.F. in volts
40.3	0
200.0	0

The electrometer needle drifts slowly in one direction and then in the other, but it is concluded that this is due to stray currents or else to slight impurities in the cell. Accordingly the zeta potential for a carbon tetrachloride-aluminum oxide interface is zero.

TABLE XVII

Summary of Data in Tables II to XVI

Table	Liquid	ζ-potential	*qd* ($\times 10^6$)	Unbalanced orientation of molecules in interface %
II	Acetic acid	+ 39.4	6.52	11.4
XI	n-Propionic acid	+ 18.66	1.67	2.34
XII	n-Butyric acid	+173.7*	13.0	35.2
XIII	n-Valeric acid	+ 12.1	0.84	—
XIV	n-Caproic acid	+ 29.0	2.48	—
III	Methyl acetate	− 21.7	3.88	4.88
IV	Ethyl acetate	− 24.8	4.14	5.05
V	n-Propyl acetate	− 19.2	3.17	3.75
VI	n-Butyl acetate	− 20.6	2.75	3.27
VII	n-Amyl acetate	− 9.53	1.26	1.45
VIII	Ethyl formate	+113	21.2	24.1
IV	Ethyl acetate	− 24.8	4.14	5.05
IX	Ethyl n-propionate	− 10.8	2.90	3.56
X	Ethyl n-butyrate	− 32.1	4.36	—
XV	Benzene	0	0	0
XVI	Carbon tetrachloride	0	0	0

* This value may be +17.37. A value of 173.7 is obtained providing the value for κ_s is 4.07×10^{-9} (Table XII). The corresponding values for propionic acid and valeric acid are 5.77×10^{-10} and 4.06×10^{-10} respectively. *If an error was made in recording* the resistivity data on butyric acid and the exponents were 10^{-10} instead of 10^{-9} the value of ζ would be 17.37 instead of 173.7. This appears probable.

If ζ were 17.37, the value for qd would correspondingly be 1.30 and the "unbalanced" orientation would be 3.52%. The series would thus become essentially regular. Since a slight change in the absolute specific conductivity makes these large changes in the determined constants, it is perhaps permissible to call attention to the data of Fairbrother and Balkin,[10] who, in their electro-endosmotic study of glass-organic liquid interfaces, state that "a value of (κ) = $< 1 \times 10^{-8}$ indicates that the conductivity of the liquid in question was too small to be measured, with the apparatus in use at the time." Propionic acid is one of the liquids which they list as having a specific conductivity of less than 1×10^{-8}. While it is not specifically stated, presumably they used $\kappa = 1 \times 10^{-8}$ in calculating their values of ζ. Unfortunately, their data as presented do not permit a recalculation to determine this point. If we were to use for our data a value of $\kappa_s = 1 \times 10^{-8}$, instead of 5.77×10^{-10} as experimentally determined, we should have found that $\zeta = + 322.9$ instead of the value of + 18.66 m.v. which we report.

Discussion of Results

The streaming potentials obtained in these studies are greater than those observed by others, but it is to be emphasized that this is not due to any peculiarity in the structure of the compounds investigated. The specific conductivity of the liquid in the diaphragm is approximately the same as that of the liquid in bulk. No effort has been made to make an exact determination of the amount of surface conductance, but the results indicate that it is not large, which is to be expected, for the specific surface of the aluminum oxide is relatively low. Martin and Gortner[3] report specific conductivities which are more than a thousand times as great as the conductivities of the liquids in bulk. This can be accounted for only by the fact that the cellulose composing the diaphragm plays a major rôle in the conduction of the current between the electrodes. Aluminum oxide is evidently a "non-conductor." The ζ-potential values which we report are of the same magnitude as theirs. From a consideration of the ζ-potential equation, it is evident that H must vary inversely as κ_s, the other terms remaining constant. Accordingly, the explanation for the large streaming potentials is merely that the aluminum oxide composing the diaphragm does not contribute appreciably to the conductivity of the system.

It is stressed that ζ-potential values obtained from determinations on diaphragm material which carries a large part of the total current in the cell are not thereby invalidated. However, it is evident from the data of Martin and Gortner that the use of cellulose in surface conductance determinations for liquids of specific conductivities less than 1×10^{-6} is inadvisable. Surface conductance is not appreciable in the case of liquids of large conductivities. Accordingly, it is evident that in surface conductance determinations, cellulose can be used only under limited conditions.

The ζ-potentials of the entire series of esters investigated, with the exception of ethyl formate, are negative (the sign applying to the aluminum oxide). The anomalous behavior of ethyl formate may be explained by assuming that it behaves not only as an ester but also as an "aldehyde." It is well known from the reactions of organic chemistry that the formates behave abnormally in respect to the other esters, and our results are in agreement with this fact. Not only is the sign of the charge reversed, indicating a reverse orientation of the dipoles, but the per cent of "unbalanced" oriented molecules is much greater indicating that the "aldehydic" group, with its secondary valencies, tends to promote a specific molecular orientation.

Figs. 3 and 4 show a slight but unmistakable effect of odd and even numbers of carbon atoms on the ζ-potential. A similar effect has been known for a long time in the case of some of the physical properties of the fatty acids, and it has led to the formulation of a zigzag structure for the carbon chain. This has been verified in a few cases by X-ray studies. Mueller[13] has shown that this picture requires a difference in the packing at the ends of the molecules.

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[13] Proc. Roy. Soc., 124A, 317-321 (1929).

In general, the electric moment of the double layer decreases with increasing length of the chain. The effect of alternate carbon atoms is felt in the case of this function also. For both series of esters, the "unbalanced" orientation of the molecules adsorbed at the interface decreases as the carbon chain increases in length. It should be stressed, however, that the calculations involved in the determination of the degree of orientation at the interface are based on the assumption that the distance between the centers of the charges at the interface are the same as between the dipoles of the molecule under the conditions of the dipole-moment determination. This may be far from the case, and accordingly the values must be interpreted with this in mind.

The data for the acids are not shown in a graph because of the question which is raised in the footnote to Table XVII as to the values for the constants for butyric acid. In general, however, the acid series shows similar trends to the ester series, excepting for the sign of the charge, which is positive for all of the acids and negative for all of the esters with the exception of ethyl formate. We do not believe that the anomalous behavior of ethyl formate is due to formic acid formed by hydrolysis, since special precautions were taken to ensure the purity of this ester.

The absence of a streaming potential at any pressure for either benzene or carbon tetrachloride indicates that the molecules of these compounds are entirely symmetrical. This confirms the earlier observations of Martin and Gortner[3] who found that no streaming potential was produced at a benzene-cellulose interface, and those of Fairbrother and Balkin[10] who observed no electro-endosmosis of benzene and carbon tetrachloride through a glass diaphragm.

Summary

The streaming potentials of aluminum oxide-liquid interfaces involving 15 pure organic liquids have been determined. The ζ-potential, the electric moment of the double layer, and the degree of orientation have been calculated. The data support the following conclusions:

1. The streaming potential increases linearly with the pressure, as is demanded by theory.

2. For a series of normal aliphatic esters, the ζ-potential and electric moment of the double layer decrease as the number of carbon atoms increases.

3. The "immobile" side of the double layer is negatively charged for all esters examined with the exception of ethyl formate (+), and positively charged for the series of n-aliphatic acids.

4. Ethyl formate behaves abnormally both as to sign and magnitude of the electrokinetic effect. This is probably due to the reactivity of the "aldehyde" group.

5. An alternating effect of the odd and even number of carbon atoms is observed on the ζ-potential and on the electric moment of the double layer.

6. The percent of "unbalanced" molecules oriented in the interface decreases with increasing length of the carbon chain.

7. The complete symmetry of the benzene and carbon tetrachloride molecules is evidenced by the lack of streaming potentials.

8. There is an almost exact parallelism between the electric moment per unit area of the double layer at the interface and the percentage of "unbalanced" oriented molecules in the interface. This observation leads to the conclusion that the electrokinetic forces at a solid-organic liquid interface are due to the electrical dissymmetry of oriented organic molecules and extends the molecular orientation, theory of Hardy, Harkins, Langmuir, Adam, *et al* to include surface electrical forces as well as surface tension and interfacial tension.

9. These studies confirm the suggestion of Martin and Gortner that streaming potential technic may be used to advantage in problems primarily concerned with the structure of organic molecules.

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A CORRELATION OF STREAM POTENTIALS AND SURFACE CONDUCTANCE

BY H. L. WHITE, FRANK URBAN AND E. A. VAN ATTA

At the 1931 Colloid Symposium we reported[1] that the stream potential of pyrex capillaries with 5×10^{-4} N KCl was independent of capillary size down to a bore of about 0.01 mm. Below this bore the potential decreased, being found about 75% as great with a 0.005 mm capillary as with large capillaries, *i.e.*, of 0.1 mm. McBain and Peaker[2] had found a specific surface conductance of 1.3×10^{-7} mhos at an interface of pyrex and 1×10^{-3} N KCl; by interpolation from their data we calculate that this would be not less than 1×10^{-7} mhos for 5×10^{-4} N KCl. If the mean conductance (resultant of volume and surface conductances) calculated on the basis of McBain and Peaker's data is put into the stream potential equation $E = \zeta PD/4\pi\eta\kappa$ the calculated stream potential for a 0.005 mm capillary with 5×10^{-4} N KCl would be only 8.4% of that with a large capillary in which surface conductance can be neglected. This discrepancy might have any one or all of three explanations, 1, that McBain and Peaker's surface conductance figures are too high, 2, that the classical stream potential equation does not hold in the smaller capillaries and/or, 3, that our previously reported stream potential figures for small capillaries are too high. We are now convinced that all three explanations hold.

First, we have shown[3,4] that the specific surface conductance with pyrex and 5×10^{-4} N KCl is only 2.24×10^{-9} mhos, about 1/45 as great as found by McBain and Peaker. If the classical stream potential equation holds this conductance would make the stream potentials with 0.005 mm capillaries about 75 to 80% as great as with large capillaries, as we[1] had found to be the case. This agreement seems to be a gratifying confirmation of our stream potential results on the smaller capillaries. We now recognize, however, that our figures of last year on stream potentials in the smaller capillaries are erroneous and that the apparent agreement is merely a coincidence. The error was due to our using a paper-paraffin condenser in the stream potential measurements. For the surface conductance work[4] a standard condenser was essential. Stream potential determinations have been repeated on capillaries of various sizes using the standard 1 mf. mica condenser obtained since last year's report. It is found that the values for the larger capillaries, down to about 0.03 mm diameter, are correct as previously reported; below this bore the potentials fall off.

With the smaller capillaries the potentials are not only very much lower than with the larger, but much less satisfactorily reproducible. It had been

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[1] White, Urban and Krick: J. Phys. Chem., **36**, 120 (1932).

[2] McBain and Peaker: J. Phys. Chem., **34**, 1033 (1930).

[3] White, Van Atta and Van Atta: J. Phys. Chem., **36**, 1364 (1932).

[4] White, Urban and Van Atta: J. Phys. Chem., **36**, 1371 (1932).

noted and reported last year that with the smaller capillaries reproducibility of results was much less satisfactory. This is now known to be due to residual charges on the paraffin condenser; the lack of reproducibility with the smaller capillaries as reported in the present paper is not due to any fault in the method of measurement but to actual changes in the capillaries. It has been found that the paraffin condenser gives the same readings as the mica with resistances up to about 10^9 ohms. With higher resistances the potential readings with the paraffin condenser are too high and variable due to variations in the amount of residual charge. With the mica condenser also the readings with the smaller capillaries vary from one experiment to another but consecutive readings agree. Even with the paraffin condenser consecutive readings may show excellent agreement, giving a false sense of security. Only after beginning to use the mica condenser and finding that a small capillary which might show a potential of 600 to 800 mv. with the paraffin condenser would at the same time show from 0 to 200 mv. with the mica did we realize that our earlier figures on small capillaries, with the paraffin condenser, are too high, although those on the large capillaries are correct. In Table I are shown a few stream potentials with the mica condenser.

TABLE I

Cap. no.	Length cm.	Diameter mm.	Stream potential mv./cm. Hg	
			2.5×10^{-4} *N* KCl	5×10^{-4} *N* KCl
58d	1.1	0.0964	31.4	15.4
59	4.66	0.0405	32.0	15.6
57a	1.97	0.039	31.0	
63a	0.25	0.0058	1.6	
60a	0.94	0.0055	5.8	
61	0.76	0.0053	0.0	
70a	0.13	0.0050	0.0	2.2
69a	0.34	0.0047	9.2	2.0

The stream potentials on the smaller capillaries are much lower than can be accounted for on the basis of the classical stream potential equation by the specific surface conductance of 2.24×10^{-9} mhos which we have found; they are rather of the magnitude expected if McBain and Peaker's values are correct. We thus have the paradoxical situation that with our surface conductance value the classical stream potential equation gives the stream potentials for small capillaries which we recorded last year but which are erroneously high, while the equation with McBain and Peaker's value for surface conductance gives stream potentials of about the value reported in this paper, which we believe to be correct. Since we can find no fault with our value for specific surface conductance we conclude that the classical equation does not hold in the smaller capillaries.

It must be pointed out that the validity of the low stream potential values for small capillaries reported here depends upon the assumption that these capillaries have been satisfactorily treated. We have exerted every possible effort as to cleanliness of water, alternating periods of evaporation and condensation during steaming, protection of capillary from dust, etc., to ensure that the state of the walls of these small capillaries is the same for a stream potential experiment as it is with the larger capillaries. Furthermore, we have found that a brief period of heating a large capillary in a Bunsen flame, after it has had hot water sucked through it for an hour, will usually give a stream potential about the same as that after steaming. When a small capillary is so heated it still shows the low stream potential value, just as after steaming. We must state, however, that we cannot have the same degree of conviction regarding the adequacy of the steaming treatment with the small capillaries as with the large. When, however, a number of treatments and determinations are carried out on a given capillary and in no case does the stream potential exceed 30% of that shown by a large capillary it seems probable that the low values are not purely fictitious.

Reichardt[5] has attempted to develop an equation to express the influence of capillary diameter on the stream potential. His corrections do not bring the values down to those observed by us on the smaller capillaries. His equation $E' = E(1 + J_o/J_q)$ is equivalent merely to substituting for the bulk conductance the true conductance, *i.e.*, resultant of surface and bulk conductances, of the solution in the capillary. His correction for the departure from laminar flow suffered in the initial segment of a capillary reduces the stream potential in even a 0.005 mm capillary by only a few per cent. Thus, for a capillary of 0.005 mm diameter and 4 mm length his equation (17a), using a Reynolds number of 1000, gives $\chi_1 = 0.92$, *i.e.*, the stream potential would be lowered by only 8% due to this factor. We are not yet in a position to present a theoretical treatment of our stream potential values on the smaller capillaries.

Briggs[6] has pointed out that surface conductance may vary independently of zeta potential and has concluded that surface conductance is therefore not ionic conductance. He suggests that the effects of salts upon surface conductance are a function of their effects upon the equilibrium between monohydrol and polyhydrols. The former is supposed to be an electronic conductor; varying the nature or the concentration of ions affects surface conductance by affecting the concentration of monohydrol in the double layer. Briggs finds that the surface conductance with the tri and tetravalent cations, Al^{+++} and Th^{++++}, after passing through a maximum falls off with increasing concentration. This is attributed to their decreasing the concentration of monohydrol. Urban and Daniels[7] have found, however, that bivalent cations decrease the partial specific heat of water more than do monovalent cations. The presumption is that the effect would be still more marked with tri and tetravalent cations. A decrease in specific heat indicates, *inter alia*, a decrease in polyhydrol concentration. This finding speaks against Briggs' view that polyvalent ions reduce the monohydrol concentration.

With KCl Briggs found that surface conductance increased continuously with concentration while zeta passed through a maximum and then fell off

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[5] Z. physik. Chem., 154, 337 (1931).

[6] Colloid Symposium Monograph, 6, 41 (1928).

[7] Urban: J. Phys. Chem., 36, 1108 (1932)

continuously. This lack of correlation, as well as the findings with polyvalent ions, led him to the statement that surface conductance is not a function of the zeta potential. The thesis developed in the present and the accompanying paper is that surface conductance is a function of zeta in the following sense, that a correlation between surface conductance and zeta exists only provided that the essential conditions for exhibiting a normal zeta potential are established. In the case of glass capillaries, with the stream potential taken as an index of zeta, this means that the capillary must be of at least 0.016 to 0.02 mm. diameter and must have been subjected to a standardized treatment such that a maximum stream potential is developed.[8] If a capillary of proper size is so treated it will show with 5×10^{-4} *N* KCl a stream potential corresponding to a zeta potential of about 120 mv. and a specific surface conductance of about 2.24×10^{-9} mhos. If the capillary is allowed to stand in the solution for several days or if it is used without having been first treated it will show a much lower zeta potential, which may drop even to zero, with practically no change in surface conductance. This looks like a failure of correlation between surface conductance and zeta potential. If, however, a normal zeta potential is established, the charge density calculated from this and the surface conductance calculated from the charge density, assuming normal viscosity, mobility and dielectric constant, the surface conductance so calculated agrees with the observed. We have interpreted these facts as meaning that with the untreated capillary the diffuse layer is absent or reduced while with the treated capillary the initially existing diffuse layer gradually collapses into the Helmholtz layer. The sum of the charges in the entire double layer remains constant; the ions in the Helmholtz layer can conduct electrical current but cannot contribute to stream potential, *i.e.*, they can move in an electric field but not under hydrostatic pressure. The surface conductance is, therefore, unaffected by the distribution ratio of ions between diffuse and Helmholtz layers, but the zeta potential depends upon this distribution. If we establish the proper conditions practically all of the cations at a glass-aqueous interface are in the diffuse layer with concentrations of KCl not greater than 10^{-3} *N*. When a normal, *i.e.*, maximum for that system, zeta potential exists the cation conductance in the diffuse layer (with concentrations of KCl not greater than 10^{-3} *N*) is therefore practically equivalent to the total cation conductance and can be calculated from the zeta potential.

With increasing concentration, where it is no longer true that practically all of the cations are in the diffuse layer, one can still calculate surface conductance from normal, *i.e.*, maximum for that system, zeta potentials if the distribution of cations between diffuse and Helmholtz layers is first calculated

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[8] The determination of both surface conductance and stream potential on one and same capillary is difficult but not impossible. The percentage of error is rather large since, if a capillary of diameter greater than 0.02 mm is used the ratio of surface to volume is too low for the most accurate determinations of surface conductance while if the diameter is less than 0.016 mm the stream potential is likely to be too low. Numerous determinations on a capillary of 0.0186 mm diameter have shown marked fluctuations in stream potential depending upon its treatment, while the surface conductance remained constant. Furthermore, the type of treatment known to be essential to the establishment of a normal stream potential in large capillaries is known not to be essential to the maintenance of a constant surface conductance in small capillaries.

according to the method outlined in the accompanying paper, and allowance made for the conductance of ions which are no longer in the diffuse layer.

While affording a satisfactory explanation of both Briggs' and our results with monovalent cations this concept at first thought seems inadequate to account for Briggs' finding that with polyvalent cations the surface conductance progressively decreases as concentration and zeta potential increase. We are not yet ready to discuss this situation fully. Insufficient knowledge of the work functions of adsorption of these ions makes it impossible to calculate satisfactorily the distribution between the diffuse and the Helmholtz layers. Until such calculations are possible we cannot judge of the applicability of our equations to the case of polyvalent cations. We may point out that McBain and Peaker, working with pyrex surfaces, did not find a decrease in surface conductance on increasing the concentration of $AlCl_3$, as did Briggs with a cellulose diaphragm. They found that the increase in conductance on increase of concentration was even greater with $AlCl_3$ than with KCl. Furthermore, Bull and Gortner[9] working with cellulose diaphragms found with $ThCl_4$ a fall in surface conductance followed by a rise, within the same range of concentrations used by Briggs. We are now investigating the surface conductances at pyrex surfaces of various concentrations of salts with ions of different valences but are not yet prepared to report our findings.

Summary

1. The stream potentials with capillaries of 0.005 mm diameter are from 0 to 25% as great as with large capillaries, instead of 75 to 85% as great, as was reported last year.

2. These low figures cannot be accounted for by the classical stream potential equation or by any modification so far proposed. The possibility that unavoidable inadequacies of treatment of the smaller capillaries may be in part responsible for these abnormally low values cannot be excluded but it is believed that the low values are not entirely fictitious.

3. A necessary and sufficient condition to a correlation between surface conductance and stream potentials is that the conditions essential to the exhibition of a normal stream potential be established. The zeta potential may fluctuate with no change in surface conductance but if a normal zeta is established surface conductance can be calculated from it and vice versa.

4. Briggs' findings on monovalent cations which led him to the conclusion that surface conductance is not a function of the zeta potential can be interpreted as indicating that in his experiments the diffuse layer is less pronounced and varies more with concentration than is the case at glass surfaces; under these conditions the zeta potential is not an index of the charge density until the distribution of charges between the components of the double layer is determined. The case of polyvalent cations is being further investigated.

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[9] J. Phys. Chem., 35, 307 (1931).

APPLICATION OF THE DOUBLE LAYER THEORY OF OTTO STERN. I

BY FRANK URBAN AND H. L. WHITE

In recent communications, surface conductance and stream potential measurements in Pyrex capillaries of various sizes were reported.[1] Capillaries of from 0.00182 to 0.10 mm bore were used, macroscopic surface to volume ratios as high as 22,000 to 1 being obtained as compared with 1600 to 1 by McBain, Peaker and King.[2] A specific surface conductance for Pyrex glass and 0.0005 *N* KCl of 2.24×10^{-9} mhos was found, as compared with an extrapolated value of 1×10^{-7} by McBain and Peaker, their figure being 45 times as great as ours. If, as we believe, McBain and Peaker's figures for surface conductance are erroneously high, McBain's arguments against the ζ-potential concept lose their weight.[3]

A further confirmation of the ϵ—ζ-potential concept of Freundlich would result, if it could be shown that there is a quantitative correlation between surface conductance and ζ- and ϵ-potentials, respectively. In the present paper, it will be shown that surface conductance and ζ-potential are related. The second relation, namely between ϵ-potential and surface conductance, will be dealt with in a subsequent publication.

In order that ζ-potential values calculated from surface conductance might be compared with those obtained by a second independent method, we selected the stream potential technique. ζ-potentials calculated from stream potentials are in agreement with the Helmholtz theory, providing the capillary radius is approximately $\geqq 10\ \mu$ and that Poiseuille's law is obeyed. This view is based on our experimental findings.[4] As the Helmholtz equation breaks down below a capillary radius of about 10μ, it follows that in this region it is not permissible to calculate absolute values of ζ-potential or electric moment by means of this equation.

Double Layer Equation of Otto Stern[5]

The theoretical bridge between surface conductance and ζ-potential is to be found in Stern's equation which describes the structure of an electrical double layer due to ionic adsorption at phase boundaries. It represents a synthesis of the Helmholtz and Gouy double layer concepts.[6] According to this equation:

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[1] White, Urban and Krick: J. Phys. Chem., **36**, 120 (1932); White, Van Atta and Van Atta: **36**, 1364 (1932); **36**, 1371 (1932).

[2] J. Am. Chem. Soc., **51**, 3294 (1929).

[3] J. Phys. Chem., **34**, 1033 (1930).

[4] Loc. cit.

[5] Z. Elektrochemie, **30**, 508 (1924).

[6] For a discussion of the equation, see Buzagh: Kolloid-Z., **52**, 57 (1930); Freundlich: "Kapillarchemie," **1**, (1930); Mueller: Kolloidchem. Beihefte, **26**, 257 (1928); Langelaan: Arch. néerland. Physiol., **16**, 145 (1931) (in English).

$$(1)\quad \underbrace{K_0(\psi_0-\psi_1)}_{\eta_0} = \underbrace{FZ\left\{\frac{1}{1+\frac{1}{18\,c}e^{\frac{\Phi_+-F\psi_1}{RT}}}-\frac{1}{1+\frac{1}{18\,c}e^{\frac{\Phi_-+F\psi_1}{RT}}}\right\}}_{\eta_1}+$$

$$\underbrace{\sqrt{\frac{DRTc}{2\pi}}\left\{e^{\frac{F\psi_1}{2RT}}-e^{\frac{-F\psi_1}{2RT}}\right\}}_{\eta_2}$$

Where N Avogadro number; e charge of electron; K_0 capacity of Helmholtz condenser; ψ_0 potential drop across Stern double layer; ψ_1 potential drop across diffuse (Gouy) double layer, approximately equal to ζ-potential; η_0 excess negative charges on solid surface; F 96,500 coulombs; Z maximum number of mols of ions which can be accommodated in a unimolecular layer of 1 cm². (max. no. of ions = z); Φ_- molar energy of adsorption of anions; Φ_+ molar energy of adsorption of cations; c concentration of salt in mols per cm³; η_1 excess positive charges in Helmholtz layer; η_2 excess positive charges in diffuse layer; D dielectric constant; l_a mobility of anion; l_k mobility of cation; η_0 number of anions in inner Helmholtz layer, if the cations can be neglected.

Distribution of ions in Helmholtz and Gouy Layers.
For 5 × 10⁻⁴ M KCl/liter and Pyrex Glass

From Equation (1), it follows that

$$(2)\quad \text{Number of cations in outer Helmholtz layer} = \frac{z}{1+\frac{1}{18\,c}e^{\frac{\Phi_+-F\psi_1}{RT}}}$$

$$(3)\quad \text{Number of anions in outer Helmholtz layer} = \frac{z}{1+\frac{1}{18\,c}e^{\frac{\Phi_-+F\psi_1}{RT}}}$$

$$(4)\quad \text{Number of cations in Gouy layer} = \sqrt{\frac{DRTc}{2\pi e^2}}\cdot e^{\frac{F\psi_1}{2RT}}$$

$$(5)\quad \text{Number of anions in Gouy layer} = \sqrt{\frac{DRTc}{2\pi e^2}}\cdot e^{\frac{-F\psi_1}{2RT}}$$

The ratio of anions to cations in the inner Helmholtz layer is perhaps of the order of e^{Φ_+}/e^{Φ_-}.

In order to simplify the calculations, the cations in the inner Helmholtz layer, also the ions of (2), (3), and (5) can be neglected. Equation (1) reduces in that case to

$$(6)\quad \eta_0 = \sqrt{\frac{DRTc}{2\pi e^2}}\cdot e^{\frac{-F\zeta}{2RT}},\ \text{and, therefore}$$

$$(7)\quad \text{Surface conductance/cm}^2 = \sqrt{\frac{DRTc}{2\pi e^2N^2}}\cdot e^{\frac{-F\zeta}{2RT}}(l_a+l_k).$$

Equation (7) implies that anions as well as cations are mobile. This assumption is in conflict with the well-known electrosmose equation, where it is assumed that the ions of the inner Helmholtz layer are fixed.

It will now be shown that the simplification leading to (7) is permissible. (4) and (5) will be evaluated first. The only unknown in these equations is ζ ($\cong \psi_1$) which can be calculated from stream potentials. The average stream potential observed by Lachs and Biczyk[7] (by interpolation) with 5×10^{-4} M KCl was 16.4 mv/cm Hg; that observed by White, Urban and Krick for large capillaries, was 17 mv/cm Hg. Taking the average of these two sets of data we get 16.7 mv/cm Hg. Average temperature is taken as 22°C. Since for large capillaries, no size corrections are necessary, the calculation for ζ is made by the Helmholtz equation.[8]

$$(8)\quad \zeta = \frac{1.67 \times 10^{-2} \times 3.1416 \times 10^{-2} \times 7 \times 10^{-6} \times 9 \times 10^{11}}{13.6 \times 981 \times 80} = 0.124 \text{ v.}$$

Since we are here operating only in the diffuse layer, the normal value of 80 for D is used.[9] The number of cations in the Gouy layer, according to (4), equals

$$(9)\quad \sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^{7} \times 295 \times 5 \times 10^{-7}}{2 \times 3.1416 \times 2.27 \times 10^{-19}}} \times e^{\frac{9.65 \times 10^{4} \times 3 \times 10^{9} \times 1.24 \times 10^{-1}}{3 \times 10^{3} \times 2 \times 1.99 \times 4.183 \times 10^{7} \times 2.95}} = 0.96 \times 10^{13}.$$

while the number of anions, according to (5) is 0.73×10^{11}. Hence (5) can be neglected.

The evaluation of (2) and (3) requires a knowledge of z and Φ_+, Φ_-. We shall use 1.27×10^{15} for z, obtained from KCl crystal lattice measurements. As pointed out by Stern, Φ_+ and Φ_- can be calculated from $c_m = 2.3 \times 10^{-4}$ *M* KCl per liter, the concentration at which $\zeta = 0.140$ v is a maximum (data of Lachs). The result of the calculation is

$$(10)\quad \Phi_+ = 1.34 \times 10^{11}$$

$$(11)\quad \Phi_- = -1.37 \times 10^{11}$$

Substituting these values in (2), the number of cations in the outer Helmholtz layer is found to be

$$(12)\quad 5.8 \times 10^{8} = \frac{1.27 \times 10^{15}}{1 + \frac{1}{9 \times 10^{-6}} \cdot e^{\frac{3 \times 10^{2} \times 1.34 \times 10^{11} - 9.65 \times 10^{4} \times 3 \times 10^{9} \times 1.24 \times 10^{-1}}{3 \times 10^{2} \times 1.99 \times 4.183 \times 10^{7} \times 2.95 \times 10^{2}}}}$$

The number of anions per cm², according to (3), is

$$(13)\quad 3.1 \times 10^{10} = \frac{1.27 \times 10^{15}}{1 + \frac{1}{9 \times 10^{-6}} \cdot e^{\frac{-3 \times 10^{2} \times 1.37 \times 10^{11} + 9.65 \times 10^{4} \times 3 \times 10^{9} \times 1.24 \times 10^{-1}}{3 \times 10^{2} \times 1.99 \times 4.183 \times 10^{7} \times 2.95 \times 10^{2}}}}$$

(12) and (13) are negligible.

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[7] Z. physik. Chem., 148 A, 441 (1930).

[8] The Helmholtz *stream potential* equation does not conflict with Stern's double layer structure, if ζ is defined as the potential of the diffuse layer.

[9] Deubner: Ann. Physik, 84, 429 (1927), cited in Handbuch der Physik, XIII, 372 (1928); Kallmann and Doch: Z. physik. Chem., 126 A, 305 (1927).

Finally, the ratio of anions to cations in the inner Helmholtz layer being of the order e^{Φ_+}/e^{Φ_-}, we obtain by substitution

$$(14)\quad \frac{\text{anions}}{\text{cations}} = \frac{e^{2.71 \times 10^{11}}}{1}$$

These preliminary calculations indicate that the simplifications leading up to Equation (7) are permissible. Before putting (7) to the test, two important points will have to be discussed.

(*a*). The objection may be raised that the true surface of the capillaries is not known, and that it is the micro-surface which determines conductivity. A macro-surface of 1 cm^2 might perhaps, let us say, represent a micro-surface of several cm.^{2} It can be readily seen, however, that a *hap-hazard* micro-structure such as may be presumed to exist in the case of glass would leave the surface conductance unchanged.

(*b*). The preliminary calculations indicated that for 5×10^{-4} M KCl per liter $\eta_1 \langle\langle \eta_2$. This is the exact opposite of the assumption made by Stern, namely, $\eta_2 \langle\langle \eta_1$, on which he based his method of calculating Φ_+ and Φ_-. Our values of Φ_+ and Φ_-, which have been calculated according to Stern, can therefore be but a rough approximation. Nevertheless, allowance for a large error in the calculated Φ_+ and Φ_- values does not materially change the relation $\eta_1 \langle\langle \eta_2$.

Calculation of Surface conductance for 5 × 10^{-4} M KCl per liter, by (7).

(15) Surface conductance/cm^2 =

$$\sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^7 \times 295 \times 5 \times 10^{-7}}{2\pi \times 4.774^2 \times 10^{-20} \times 6.06^2 \times 10^{46}}} \cdot e^{\frac{-9.65 \times 10^4 \times 0.124}{3 \times 10^2 \times 2 \times 1.99 \times 4.183 \times 10^7 \times 295}} \cdot 150.$$

(16) Surface conductance/cm^2 = 2.4×10^{-9} mho.

The experimentally observed surface conductance is 2.24×10^{-9} mho.

The normal value of 75 for the mobility of Cl$^-$ and K$^+$ was substituted in (15).

Calculation of ζ from surface conductance. 2.5 × 10^{-4} M KCl per liter.

We find experimentally that

(17) Surface conductance/cm^2 = 1.35×10^{-9} =

$$\sqrt{\frac{80 \times 1.99 \times 4.183 \times 10^7 \times 298 \times 2.5 \times 10^{-7}}{2\pi \times 2.27 \times 10^{-17} \times 3.67 \times 10^{47}}} \cdot e^{\frac{9.65 \times 10^4 \times 3 \times 10^9 \times \zeta}{2 \times 1.99 \times 4.183 \times 10^7 \times 295}} \cdot 150$$

$$(18)\quad \zeta = \frac{0.96 \times 3 \times 10^2}{2.5 \times 10^3} = 0.11 \text{ v.}$$

The value determined from stream potential is ζ = 0.12 v. This agreement is satisfactory.

Similar calculations with 10^{-5} *M* KCl per liter, 10^{-4} *M* and 10^{-3} *M* have been undertaken. The agreement was as good as could be expected. The data have not been included in this paper, as a greater number of surface conductance determinations in solutions of the last mentioned concentrations have yet to be carried out.

Discussion

The good agreement between our calculated and observed quantities appears to justify the underlying assumptions:

(a). In an electric field, *all* ions of the double layer are mobile.

(b). The mobility of the double layer ions is close to normal.

(c). The double layer at a Pyrex/KCl-solution interface is composed of K^+ and Cl^-.

(d). The number of cations in the inner Helmholtz layer is negligible, at the KCl concentrations investigated.

The assumption of Helmholtz and von Smoluchowski that the ions on the wall (ions of the inner Helmholtz layer) are immobile, would give a calculated value of surface conductance one-half of that observed. In order to overcome this difficulty, the abnormally high mobility of 150 for K^+ would have to be postulated (as compared to a normal value of 75). It is undoubtedly less forced to attribute normal mobilities to K^+ and Cl^- and to allow both to move. At the present time, it is an open question as to how much energy is required for lateral motion of an ion along a surface.[10]

By assigning normal mobilities to both K^+ and Cl^-, the observed surface conductances harmonize with the calculated ones. This could be the case only if the double layer contained but insignificant numbers of ions other than K^+ and Cl^-.

In order to test these assumptions still further, we are determining surface conductance with other salts. Assumption (c) can be tested directly, by obtaining adsorption isotherms on Pyrex glass wool. These should also make it possible to evaluate (d).

Finally, we conclude, on the basis of the evidence presented in this paper, that Stern's concept of a variable charge governed by adsorption, is sound.

Summary

1. It has been shown that in dilute solutions ζ-potential and surface conductance are related.

2. Evidence has been adduced to show that the ions of the inner Helmholtz layer are mobile, and also

3. That the assumption $\eta_1 \gg \eta_2$ in dilute solutions made by Stern for the purpose of calculating Φ_+ and Φ_- is not justified.[11]

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[10] Private communication from Dr. Henry Eyring, Princeton.

[11] Hans Müller has raised the same objection independently. Kolloidchem. Beihefte, **26**, 282 (1928).

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. VI*

BY WILDER D. BANCROFT AND JOHN E. RUTZLER, JR.**

In previous papers comprising this series, it was shown that peptizing agents, sodium rhodanate in particular, reverse the agglomeration brought about by anesthetics and allied drugs. Human beings, dogs, rabbits, and plants, have been made to recover experimentally from anesthetics or hypnotics more quickly by the administration of a peptizing agent, given in order to counteract the agglomeration which is a part of the induced condition. To date, despite a great many ill-founded criticisms and a few badly planned experiments, the theory of reversible agglomeration stands forth as the only rational conception of the action of many drugs. Experimental support of the theory continues to come in from those who understand how to make use of a good theory. In order to secure further support of the theory that anesthesia is accompanied by reversible agglomeration of certain protein colloids of the central nervous system, experiments were carried out on goldfish, *Carassius auratus.* The limited facilities of a chemical laboratory for physiological research still enable one to perform a good many experiments with goldfish. However, no attempt was made to reach the magic number of experiments—one hundred.

At first sight, it may seem that the goldfish is structurally a simple animal upon which to experiment. Because this was not found to be the case, it seems wise to consider briefly some of the major facts of the neuro-anatomy of fishes.

Kyle[1] says: "The spinal nerves connected with the different segments are arranged in the same way as in Higher Vertebrates and there is also an internal sympathetic system. The cranial nerves are for the most part the same, with some variations in their development and importance. The VIIIth nerve, for example, is specially large and is connected with an independent centre in the medulla, the tuber acusticum. This is supplied from the general cutaneous nerves, lateral line system, as well as from the auditory organ or statocyst."

On page 159: "The simplest form of sense organ is seen in the end-buds which occur anywhere on the skin of fishes. On Higher Vertebrates these become restricted to the mouth as taste-buds. Sometimes they are raised on eminences, but most often they sink deeper into the skin and the nerve-endings become embedded in mucus or glandular tissue. Whether they are all connected with reception only, we do not know. . . ." In another place,

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** Eli Lilly Research Fellow.

[1] "The Biology of Fishes," 167 (1926).

Kyle says that the diffuse end-buds seem to be able to detect differences in the chemical nature of the surroundings.

On page 160 he says: "On the other hand the organs of the lateral line have quite a different function. . . . According to Parker these organs are not stimulated by light, heat, salinity of water, food, oxygen, carbonic acid, water pressure, currents, or sound. . . ."

"The lateral line organs seem also to be of some use both in orientation, according to the different strengths of currents on the two sides of the body, and in balancing. He found that when the pectoral and ventral fins were removed, the fish (Opsanus) showed no lack of equilibrium so long as the lateral line was left intact."

On page 141 Kyle says: "So long as a fish is alive, its internal constitution and particularly the composition of its blood are quite different from those of the surrounding medium. It is self-contained and only takes in the materials it wants to take in. . . .

"Freshwater fishes like the Carp have a much greater [osmotic] pressure within the blood than that externally; by increasing the amount of salt in the water to 10 grm. *pro mille* Portier and Duval were able to obtain equilibrium within and without; but with still further increase in the salinity the gill membrane seemed to be forced and the fish died. As the pressure of the blood also increased, though slightly, in these experiments, it would seem that a small amount of the external salts in solution is able to pass through the membrane. But this is by no means certain; and other observers think that only water is able to pass through. It is possible that the fish is able to withdraw water and salts from the tissues and thus regulate its exchanges. The Salmon, for example, does not change its osmotic pressure all at once on entering fresh water; and the Eel, when transferred from fresh to salt water, does not assume the osmotic pressure of the latter."

On page 18 we find: "But the latter organs [the kidneys] are not so well-developed in the fishes as in higher vertebrates, and thus the guanin and lime become deposited in the dermis . . . and in common with guanin lime is often present in the internal tissues of the fish, as in the retina of the eye, peritoneum, air-bladder, etc. . . ."

From these few quotations it can be seen readily that exposing fish to electrolytes and anesthetics may give rise to several phenomena, other than straightforward anesthesia and recovery. It was found almost at the outset that the problem was not simple.

In order to make sure that in the case of the fish we are dealing with protein colloids of the nervous system which respond to the electrolytes of the lyotropic series like those of the other animals with which we have dealt, swelling experiments were performed.[1] Whole, freshly excised, goldfish brains were weighed and then placed in ten percent solutions of sodium iodide, sodium chloride, and sodium citrate. After being in the solutions for periods of one, two, and twenty hours each of the brains was again weighed. From these data the percentage change in weight was computed. A positive change in weight

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[1] The authors are grateful to Dr. Robert L. Nugent for performing these experiments.

was found in the case of sodium iodide and sodium chloride, the sodium iodide causing a much greater increase in weight than the sodium chloride. In the sodium citrate solution the goldfish brain lost weight. This was found to be the case whether the hydrogen ion concentration of the sodium citrate solution was barely on the acid or on the alkaline side of the neutral point. So, sodium iodide and sodium chloride peptize goldfish brains, as they should; and sodium citrate produces agglomeration. The observed relations of the size of the different specimens bore out the swelling data, i.e., those that swelled most were largest in size.

Dr. Nugent also experimented with the electrophoresis of thoroughly macerated goldfish brains which had been washed and suspended in a buffer solution having an hydrogen ion concentration of $1 \times 10^{-6.5}$. All of the particles that were observed travelled quite rapidly toward the anode, showing that they were strongly negatively charged. This indicates that their isoelectric points were well below $[H^+] = 1 \times 10^{-6.5}$.

In performing experiments on live fish care was always taken to have the water containing the different compounds being studied at the temperature of the room. Thus, none of the observed effects was due to temperature differences. Apparently healthy fish were always used. When more than one experiment was done on a single fish, at least a week's time was allowed to elapse between the experiments. Generally, fish of approximately equal size were used. At least one check experiment was almost always performed; and sometimes many check experiments were made. The fish were not experimented upon shortly after being fed.

The first experiments were performed using amytal as the anesthetic. The anesthetic was prepared by warming an excess of sodium bicarbonate with three grams of amytal and fifty cc of distilled water. This was then diluted to two liters with tap water, and the solution filtered. The filtered solution was used as the anesthetic bath. Six goldfish were placed in this bath. One was anesthetized in fourteen minutes; and five lost consciousness in fifteen minutes. In each anesthesia experiment reported in this paper, unless otherwise stated, the fish was considered to be anesthetized when all voluntary movement ceased, and when there was no visible response to touch, a glass rod being used for testing the latter. As with mammals, it was observed that the fish passed through a stage of stimulation prior to the loss of consciousness. When, later, the effect of other anesthetics is described it will be seen that the period of excitation brought about by amytal is short, of the order of five minutes. Further, the period of stimulation can be varied greatly by changing the concentration of the anesthetic. Two of the anesthetized fish were placed in a 2% solution of sodium citrate which was made just acid to litmus paper with citric acid; two were put in tap water to be used as controls; and two were put into a 2% solution of sodium rhodanate.

The fish that were put into the sodium citrate laid on their sides, their tails extended below the line of their bodies. This is in marked contrast to their behavior in the anesthetic bath in which there was only a slight loss of normal balance. After a period of five to ten minutes the fish in the sodium citrate solution underwent what appeared to be a convulsive phenomenon; their bodies began to jerk. This did not result in propulsion through the water. These movements stopped in less than five minutes and the fish began to swim around excitedly. When left long in such a sodium citrate solution, after apparent recovery, the fish finally became more quiet than a normal fish. When the fish were transferred from the sodium citrate solution to tap water while still excited, a period of wild excitement ensued; they broke through and cleared the surface of the water so that their bodies were entirely out of water. This period of excessive excitement lasted for about fifteen seconds. The fish then lapsed back into a fairly deep narcosis during which they were balanced normally, and the rate of respiration became very low. At this stage when the fish were left in the tap water in other experiments they remained narcotized for upwards of forty-five minutes. On the other hand when they were put back into the sodium citrate solution until they became excited again, and then transferred to the water once more, and the whole process repeated several times, it was found that the fish recovered from the effects of the anesthetic more quickly than if they were only put into tap water after being narcotized. These results can be obtained most readily by preparing the anesthetic bath in the following manner. Mix one gram of amytal with one gram of sodium bicarbonate in about 50 cc. of water. Warm to about 60° and dilute to 560 cc. Adjust the pH to 9.05 – 9.4; then filter. The sodium citrate solution is best prepared by adding 18 grams of acid sodium citrate to one liter of water. Then add concentrated sodium hydroxide until the pH equals 6.0.

At the time when the fish that were treated with sodium citrate recovered, the controls were still very deeply narcotized, more deeply, in fact, than when they were removed from the anesthetic bath. They were finally brought out of the anesthesia by treating them with sodium citrate.

The fish that were placed in the two percent sodium rhodanate solution did not recover very rapidly; so they were treated with sodium citrate. However, it was noticed that while in the sodium rhodanate solution the respiration of these fish was more even and rapid than that of those in sodium citrate or tap water. Further, the fish in the sodium rhodanate solution suffered no loss of balance; they stayed on the bottom of the bowl, whereas those in the sodium citrate solution floated.

At first sight, it would seem from these results that sodium citrate arouses the fish from amytal anesthesia more quickly than plain tap water. Therefore it was decided to trace the phenomenon down. Two fish were left in a 2% solution of sodium citrate for three minutes; they became hyperexcitable. The fish were then transferred to tap water in which they became slightly depressed following hyperexcitability; they stayed in tap water for five minutes. After that the fish were put into the sodium citrate solution again for a period of three minutes; again they became extraordinarily excited in this solution. Upon being replaced in tap water they became slightly more hyperexcitable; this was followed by a slight depression. The fish were left in the tap water for 21 minutes following which they were placed in the sodium citrate for two and one-half minutes. Again, the cycle, hyperexcitability→depression→normal, was observed. The sodium citrate solution was at $[H^+] = 1 \times 10^{-6.45}$. The whole experiment was repeated several times with slight variations. In each case the result was qualitatively the same. The fish still behaved qualitatively the same when the solution was adjusted to $[H^+] = 1 \times 10^{-6.1}$ and $1 \times 10^{-7.1}$. It was observed that while in the sodium citrate solution the fish breathed spasmodically, so that they appeared to be holding their breath. It was found that a four percent solution of sodium citrate killed fish in an hour or less. So, most of the phenomena of rousing a fish from amytal anesthesia were duplicated, though in a much less striking manner, by the use of sodium citrate and unanesthetized fish.

It does not seem probable that the sodium citrate acts upon the same centers as the amytal in the above experiments. An experiment was performed which lends a great deal of credence to that idea. Two fish were anesthetized in an amytal solution. Then they were placed in an extremely dilute solution of sodium sulphate. Two aluminum electrodes were connected to a source of electricity which delivered five volts. When the fish were touched by the electrodes they were stimulated to activity. The stimulation ceased when the contact was broken. The same result was observed four or five times. This did not cause the fish to awaken truly from the narcosis. Likewise, fish anesthetized by urethane were brought out of the anesthesia more rapidly than controls by shocking them, using four volts. There is no evident reason why electric shocks should peptize the protein colloids of the nervous system of the fish.

Another fact of importance is that after allowing four or five fish to remain in a sodium citrate solution long enough to recover apparently from anesthesia, the solution becomes cloudy. In about a day the sol coagulates. This is coagulated fish slime. Likewise sodium amytal appears to do the same thing to a lesser degree. A 10% solution of sodium rhodanate will do the same thing by another mechanism in a longer time. The tearing off of the adherent slime must affect the fish.

From these data it appears quite certain that the apparent recovery brought about by sodium citrate is not due to a peptizing action upon the same substrate as that which is agglomerated by the amytal. As the theory stands, sodium citrate acts in one or both of the following ways: by the precipitation of calcium salts on the outside, and perhaps inside of the fish, thus causing stimulation; by the tearing off of the slimy coating and slight agglomeration in the skin sense-organs.

It will be evident from what follows that in some cases the important thing is the precipitation of calcium salts; and in others it is the agglomeration in the skin sense-organs and tearing off of the slimy coating.

Experiments with ether were undertaken next. In the first experiment 5.4 cc of anhydrous ether were dissolved in 1.5 liters of tap water. Two fish were placed in this solution. After eight minutes they began to swim backwards. They continued to do this for 10-15 minutes. Forty minutes after the fish were put into this solution four cc more ether were added. The bowl was kept covered during the experiment. The fish were left in the solution for another twenty minutes when all noticeable gill and mouth movements ceased. One was placed in a 2% solution of sodium citrate that was just acid to litmus; and the other was put into a 2% solution of sodium rhodanate. Both recovered at the same time. The fish were re-anesthetized in the ether solution about ten minutes later; this time they went under in five minutes.* This result permits of the conclusion either that the ether was not all out of the fish at the time that they were re-anesthetized, or that the agglomeration brought about by the ether was not entirely reversed.

From the above and several other comparable experiments in which ether was used as the anesthetic an interesting comparison with the anesthesia produced by sodium amytal can be made. Ether anesthesia, under the conditions of the experiment, has a much longer induction period. While the narcosis produced by ether appears to be deep, it does not last nearly so long as the amytal anesthesia. From the results of several experiments it appears that the fish recover from ether anesthesia in tap water in from two to four minutes; while the recovery time from amytal is of the order of one hour. When the fish are removed from the anesthetic bath and put into tap water the anesthesia appears to become deeper in the case of amytal, and lighter in the case of ether. This merely indicates that ether leaves the fish more rapidly than amytal. While making this comparison it is of interest to note that in several attempts to anesthetize fish with alcohol failure resulted. Solutions containing 1-3% of alcohol were used. In each case there was a long period of excitation, 45 minutes to two hours being required to produce anesthesia. During most of this time the fish were stimulated and swam around in an intoxicated manner. The elapsed time between the onset of depression and deep narcosis was very short in comparison to the long period of stimulation. In all of the experiments that were performed with alcohol as the anesthetic, the narcosis produced was deadly; very few fish survived alcohol narcosis. However, if the treatment was discontinued just short of the narcosis stage and the fish placed in tap water, they recovered exceedingly rapidly.

Nembutal, an anesthetic of the barbituric acid series was used in several experiments. It is closely related to amytal, but acted somewhat differently from amytal in the experiments that were conducted. In the course of exhaustive experiments on sodium amytal it was found that the pure salt when dissolved in water was toxic to the fish. Likewise nembutal, which is also a sodium salt, proved to be quite toxic to goldfish. In a 0.14% solution of nembutal it required on an average of 49 minutes to produce anesthesia. A very long period of great depression was noted before the anesthetic stage came on. Narcotized fish placed in a 2% sodium citrate solution behaved qualitatively the same as they did under amytal anesthesia. Quantitatively, they were stimulated more quickly by the sodium citrate than the fish anesthetized with amytal as previously described; the whole phenomenon of stimulation by sodium citrate was less marked. The narcosis induced by nembutal did not appear to be so deep as that induced by amytal.

While comparing different anesthetics, it is of interest to include urethane. Urethane dissolved in water to make a 0.5% solution or a 0.75% solution anesthetizes goldfish in from seven to fifteen minutes. In almost every case the tail goes out of commission as a swimming help first. Then, as a result of incoordinated movements of the pectoral fins, the fish swim backwards slowly. A period of slight stimulation is noticed prior to the onset of unconsciousness. The fish do not lose their balance entirely in any of the anesthetic solutions, as they do in sodium citrate. Recovery in tap water from urethane anesthesia requires approximately nine to fifteen minutes. The anesthesia does not appear to be very profound; but the effect is more lasting than that of ether. The toxicity of urethane is low. In one case a fish was left in the anesthetic bath for twenty minutes after voluntary movements had ceased and tactile stimulation evoked no response. Yet the fish recovered in a 2% solution of sodium citrate just as rapidly as another fish that remained in the bath only four minutes after the induction of anesthesia. The concentration of urethane in the solution affects very greatly the time required to produce anesthesia. For instance, two fish were not anesthetized in twenty minutes in a 0.2% solution of urethane; while a 3.5% solution brings about a good narcosis in less than two minutes. Large goldfish are more resistant to anesthesia by urethane than are small goldfish. Most of these observations of the action of urethane were confirmed in as many as fifty experiments.

Ether does not make a good anesthetic for the study of the recovery process under the conditions in which it was used, because the recovery period in tap water is so short. However, several important experiments were performed which will be reported here because of their bearing on the question of the mode and site of action of sodium citrate. A 1% solution of sodium citrate just acid to litmus was prepared; 12 cc of anhydrous ether were added to the solution. Two goldfish were placed in this solution; one of the fish was affected strongly almost immediately. It lost all of its liveliness and balance after a short period of excitation. After ten minutes it had nearly stopped visible breathing movements. Eighteen minutes after immersion in the solution all visible respiratory movements had ceased. The fish was put in tap water in which it recovered in two minutes. The second fish required 32 minutes to become anesthetized; this fish was placed in a 2% solution of sodium citrate just acid to litmus. It required 19 minutes to recover. In no other case of ether anesthesia was anything like such a long recovery period observed. In other experiments with ether the recovery period was always of the order of three minutes. Another experiment was performed in which ten cc of ether were dissolved in two liters of tap water. Two fish were kept in this solution until all visible signs of respiration had disappeared. There was less dyspnea when the fish were subjected to ether-water anesthesia than when the anesthetic bath contained sodium citrate. One was transferred to tap water to recover; the process required three minutes. The other fish was placed in the 2% sodium citrate solution; it recovered in one and one-quarter minutes.

So, fish did not recover in a 2% sodium citrate solution from anesthesia in a sodium citrate-ether-water bath nearly so rapidly as they did in water. Yet, fish anesthetized in a bath containing ether and water recovered more rapidly in a 2% solution of sodium citrate than they did in plain water. The fish recovered in water in the same time independently of which anesthetizing bath was used. The time for the induction of anesthesia in the two solutions was of the same order. If sodium citrate was acting to peptize the substrate that is agglomerated by the ether, it should have taken considerably longer for the fish to become anesthetized in the sodium citrate-ether-water solution than in the ether solution. This was not the case. Further, if the above were the case the fish would have recovered more rapidly than it did in sodium citrate after being narcotized in the sodium citrate-ether-water bath. So, the sodium citrate was not acting as a peptizing agent. Still the sodium citrate was not acting as a strong agglomerating agent for the substrate most affected by ether, because fish recovered more rapidly from plain ether anesthesia in a 2% sodium citrate solution than they did in tap water. The data do not offer any evidence that the sodium citrate and ether were acting upon the same substrate. The explanation of the results seems to be that the sodium citrate stimulated the fish by precipitating calcium salts thus arousing it from the light anesthesia that it had undergone. In the case of the fish that was subjected to sodium citrate-ether-water anesthesia the sodium citrate brought about stimulation by the precipitation of calcium salts while the fish was still in the anesthetic bath; so that immersion in sodium citrate after the induction of anesthesia did not revive the fish quickly. The fish in the sodium citrate-ether-water bath came to the top of the solution very shortly after being placed in the bath; there was distinct evidence of loss of balance. This is an indication that the sodium citrate was operating upon the sense organs on the outside of the fish, causing a slight agglomeration there. Also, it undoubtedly acted to agglomerate the slime on the outside of the fish. So, the theory of reversible agglomeration has not met defeat.

In another experiment 15 grams of magnesium sulphate (an anesthetic) were dissolved in a liter of water and five cc of ether added to the solution. Two fish were placed in the solution. Eighteen minutes later they were on their sides at the surface of the water. One became anesthetized in 22 minutes and the other in 31 minutes. Each of the fish was put into tap water upon becoming anesthetized. The fish that was anesthetized first recovered in four minutes; while the other fish recovered in four and one-half minutes. As they do in sodium citrate solutions, these fish exhibited a loss of balance. The recovery time was slightly longer in both cases than that which was observed in several experiments in which ether alone was the anesthetic. This experiment illustrates two things. In the first place, the magnesium sulphate deepened the anesthesia, as a result of its own agglomerating action. Secondly, from the loss of balance and the rise to the surface, agglomeration in the peripheral sense organs can be inferred. Calcium precipitation may have played a part here.

Mention has been made of the fact that a long series of experiments was performed with urethane as the anesthetic. In urethane solutions the usual stimulation corresponding to the initial stages of agglomeration is observed. It would be redundant to set down the experimental details of all of the work on urethane anesthesia and the process of recovery therefrom; for that reason, except in some special cases, only the general results will be cited. Most of these results have been checked several times, thus eliminating the factor of biological variation. The general procedure was to anesthetize the fish in a 0.5 or 0.75% solution of urethane in tap water. In order to make more nearly certain that the anesthesia was uniform in depth, the fish were left in the urethane solution from two to seven minutes after voluntary movement had ceased and the fish no longer responded to mechanical stimulation with a glass rod. It will be remembered that the recovery phenomenon apparently was not affected by a 20 minute sojourn in the anesthetic bath after the induction of anesthesia.

It was demonstrated that a 2% solution of sodium citrate at an $[H^+] = 1 \times 10^{-6.45}$ reduces the recovery time very greatly. In such a solution the recovery time varies between 30 seconds and two and one-half minutes. Upon removing the fish from the sodium citrate solution and placing them in tap water a period of hyperexcitability is noticed. This is followed by a short depression. The phenomenon is qualitatively the same as that observed under similar conditions using amytal for the anesthetic. The quantitative difference is probably due to the difference in depth of anesthesia, that produced by amytal being much deeper. Under special conditions urethane anesthesia and the recovery therefrom can be prolonged greatly. As has been pointed out, the citrate part of the molecule is responsible for the precipitation of calcium probably largely in the peripheral nerves of the fish, an accompanying phenomenon being agglomeration on the outside. This stimulation results in more rapid recovery of the fish.

Likewise, it was found that a 2% solution of sodium tartrate revives the fish more rapidly than they return to normal in tap water. The recovery is not so rapid as that brought about by sodium citrate. Hyperexcitability is not noticed when the fish are returned to tap water after being in sodium tartrate; but there is a very short period of depression. Now, sodium tartrate is next to sodium citrate in the lyotropic series. That means that its agglomerating action on the peripheral part of the fish will be less than that of sodium citrate. So it appears that calcium precipitation is not the whole story. Sodium tartrate acts both to precipitate calcium and produce a slight peripheral agglomeration. It should be pointed out that this agglomeration produces stimulation because it is so slight, just as the first stage of anesthesia is that of stimulation.

Now, with magnesium citrate we have an agglomerating cation as well as an agglomerating anion. As a result placing fish anesthetized by urethane in a saturated solution of magnesium citrate delays their recovery.

In a series of experiments using a 0.75% solution of urethane to produce anesthesia and eighth-molar solutions as recovery media, it was demonstrated that sodium bromide increases the rate of recovery from the anesthesia. It did not work so rapidly as sodium citrate and sodium tartrate; however, there is no question but that sodium bromide is a peptizing agent. In this case, there can not be agglomeration produced by the sodium bromide under ordinary conditions so far as one can see. It seems reasonable to assume, therefore, that sodium bromide acts to peptize the substrate that is agglomerated by the urethane.

The calcium-precipitating action of the sulphate radical of sodium sulphate was manifested in one experiment. In this case the fish recovered rapidly in a solution of that salt. Another experiment failed to show this up very clearly.

A study of the cations, still using eighth-molar solutions, revealed the fact that aluminum chloride apparently brings the fish out of anesthesia more rapidly than sodium chloride, which in turn is more effective than calcium chloride. This situation requires elaboration. The calcium chloride solution killed three out of four of the fish after they apparently had recovered from the anesthesia. One fish hemorrhaged in the solution. The order of recovery time was approximately: Al_2Cl_6, 1½ minutes; NaCl, 4 minutes; $CaCl_2$, 8½ minutes. The case of sodium chloride is not out of the ordinary; the chloride ion acts as a peptizing agent to hasten the recovery. With calcium chloride we have a weak agglomerating cation, therefore the delay in recovery. Fish generally recover from urethane anesthesia in about this length of time when placed in tap water. The calcium ion can be assumed to be acting to stimulate by a slight agglomeration on the outside of the fish. With aluminum chloride the situation is slightly different, for the trivalent aluminum ion appears to cause quite a bit of stimulation by agglomeration of protein colloids in the peripheral sense-organs. Upon transferring the fish from the aluminum chloride solution to tap water, hyperexcitability is noticed. The fish swim rapidly and blindly at the surface of the water. They are not so apt to become excited while in the aluminum chloride solution as when they are in a sodium citrate solution. The fact that the aluminum ion acts to stimulate the fish on the outside rather than acting directly to lessen the narcosis can be illustrated by an experiment with sodium amytal as an anesthetic and aluminum sulphate as the recovery agent. The anesthetic solution was prepared by dissolving one and one-half grams of sodium amytal in a liter of water and adding eight cc of 0.236 N HCl. The fish was placed in M/20 aluminum sulphate solution; after 11 minutes, it did not appear to have recovered. Upon being transferred to tap water, the fish began to swim around at the surface in circles touching the side of the container. It continued to do this for a couple of hours, around and around, always in the same direction, never leaving the side of the container, never ceasing to swim. Normal fish do not perform that way. So, it appears that aluminum sulphate and sodium citrate stimulate anesthetized fish without necessarily bringing them back to normal, when the anesthesia is deep.

Two fish were anesthetized in a 0.5% solution of urethane; they were left in the solution for four minutes after the induction of anesthesia. The fish were then placed in a very dilute solution of sodium sulphate, one or two small crystals of the salt in a liter of water. The fish were shocked intermittently using four volts, direct current, the application being made with wide aluminum electrodes. Each shock stimulated the fish and caused it to wriggle and swim a short distance. It became continually more sensitive to the current. At the end of three minutes it continued to swim without the shocks. The second fish responded in the same manner, taking four minutes to recover.

So, by electrical stimulation fish can be wakened abnormally rapidly from urethane anesthesia; and electrical stimulation probably does not result in peptization.

Using a 1% solution of urethane to anesthetize fish, it was demonstrated that the fish recover more rapidly in Ringer's solution than in distilled water. This is presumably due to the peptizing action of the chloride ion. Likewise, fish anesthetized in a 3.5% solution of urethane dissolved in Ringer's solution recovered more rapidly in an isotonic sodium chloride solution than they did in distilled water.

Approximately isotonic solutions of sodium tartrate, sodium rhodanate and aluminum sulphate were prepared, using as a basis 0.9% sodium chloride solution, and used as recovery media. The recovery phenomena were not essentially different from the observed effect of eighth-molar solutions. From this it can be concluded that osmotic pressure differences do not play an essential rôle in the recovery process.

Experiments were performed in which the anesthetic was injected into the fish. By way of illustration, 0.5 cc of a 10% solution of urethane was injected into the peritoneal cavity of an 8-gram fish. The fish was anesthetized deeply in 11 minutes. It did not recover from the anesthetic in 78 minutes. Thus, the anesthesia was much deeper than is usual when urethane is dissolved in the water. Other experiments were performed in which the fish were deeply anesthetized by a 0.75% solution of urethane, dissolved in Ringer's solution and isotonic salt solutions were injected to produce recovery. Not enough experiments were performed to be certain of the results. Fish of approximately equal weight were used. In each case 0.5 cc of the isotonic salt solution was injected. Sodium rhodanate produced excitement in the fish most quickly, one minute: aluminum sulphate required three minutes; and sodium tartrate required four minutes. With no injection the fish recovered in four minutes. The recovery of the fish injected with aluminum sulphate was not attended by circular swimming. So, the action of this salt internally appears to be different from its action externally.

Fish anesthetized by sodium amytal became wildly excited after one minute in a 0.1 M solution of sodium carbonate. There was further great excitement when the fish was transferred to water. Here we have both calcium precipitation and peptization by hydroxyl ions. Two more transfers to the sodium carbonate solution resulted in death. Another fish made a good and rapid recovery in a 0.1 M sodium salicylate solution.

Now, if calcium precipitation is largely responsible for the stimulating action of sodium citrate, reducing the amount of calcium in the fish should result in diminishing the action of that salt in producing the artificial recovery from anesthesia that has been described. Also, if the calcium-precipitating action is reduced, the agglomerating action of sodium citrate should become more apparent and sodium rhodanate should be more effective than sodium citrate in bringing the fish out of anesthesia. In an attempt to realize these predictions, fish were placed in a bowl; and distilled water was run in continuously for a period of about five days. A total of more than 54 liters of distilled water was run through. The fish container was a 1-liter beaker. The fish were not fed during the process in order to avoid the introduction of calcium. The first fish subjected to this process died in convulsions in about four days. It may be that a tetany similar to parathyroid tetany resulted from lowering the calcium content of the fish. The second time that the process was carried out Ringer's solution, without calcium and magnesium chloride, was used to "dialyze" the fish on the second and third day; distilled water was used the rest of the time. Fish that were so treated were anesthetized in a 0.75% solution of urethane. It was noticed that the anesthesia was quite a bit more profound than usual. When the anesthetized fish were placed in sodium citrate (1.78% solution just acid to litmus) the phenomenon was more like that described under amytal anesthesia. The fish apparently aroused from the anesthesia, and became narcotized again when placed in distilled water. However, there was no great excitement noticed. In several experiments it was found that the 1.78% solution of sodium citrate, when it was slightly alkaline and when it was slightly acid, did not counteract the anesthesia for from 22 to 24 minutes. The fish were artificially stimulated in a shorter time than that; but they lapsed back into a good narcosis. The artificial stimulation indicates that the "dialyzing" process did not lower the calcium sufficiently. In other recovery experiments with these specially treated fish an eighth-molar solution of sodium rhodanate revived them three to five minutes more rapidly than the sodium citrate solution did. So, the peptizing action of sodium rhodanate was demonstrated clearly, and it was shown that sodium citrate indirectly stimulates fish to bring them out of anesthesia.

It was found possible to show that sodium citrate has an anesthetic-like action on these specially treated fish and that sodium rhodanate tends to counteract it. Two of the fish were placed in the above sodium citrate solution for a period of four minutes. They were highly excited in the sodium citrate solution. When transferred to distilled water they became depressed. Their sensitivity to touch was diminished; and the fin movements were incoordinated as in anesthesia. After nine minutes in tap water, when the fish were again normal in action, they were placed in the sodium citrate solution again, where they were left for four minutes. One fish then was put in water and the other in eighth-molar sodium rhodanate solution. Two minutes later the fish in sodium rhodanate was excitable to touch and was swimming around; while the other fish appeared to be anesthetized. This is not a very striking experiment; but it is definite; and sodium citrate is not a good anesthetic.

General Conclusions

1. A study of anesthesia and the recovery phenomena has been made on goldfish anesthetized by sodium amytal, ether, nembutal, alcohol, and urethane.

2. A comparison of the anesthesia produced by these compounds is made.

3. At first sight the theory of reversible agglomeration does not appear to hold because sodium citrate, sodium tartrate, and aluminum sulphate all revive the fish more rapidly than sodium rhodanate, sodium chloride and sodium bromide. Sodium salicylate and sodium carbonate also revive fish quickly.

4. Sodium bromide, sodium chloride, and sodium rhodanate all bring the fish out of anesthesia more rapidly than tap water due to the peptizing action of the anions.

5. Electric shocks bring fish out of anesthesia more rapidly than is normal.

6. Sodium citrate acts on a different substrate from that which is agglomerated by anesthetics.

7. Sodium citrate precipitates calcium, coagulates the slime on the fish, and causes agglomeration of protein colloids in some of the sense organs on the outside of the fish. This causes the fish to become stimulated, and apparently awakens them from the anesthesia.

8. Fish awakened from deep anesthesia by the stimulation produced by sodium citrate, become narcotized again when placed in tap water.

9. Aluminum sulphate stimulates fish by its agglomerating action in the outside sense organs. Fish revived by the use of aluminum sulphate behave abnormally when placed in tap water. Still the total time for recovery is short.

10. Fish that are "dialyzed" in distilled water go under deeper anesthesia in urethane than fish not so treated.

11. Fish that have been "dialyzed" in distilled water recover from urethane anesthesia more rapidly in a sodium rhodanate solution than in a sodium citrate solution.

12. Fish that have been "dialyzed" in distilled water behave as though anesthetized when placed in sodium citrate solutions. Sodium rhodanate appears to counteract this effect.

13. Osmotic pressure changes do not appear to be concerned in the recovery from anesthesia. Likewise, slight variations in acidity do not seem to make any difference.

14. Claude Bernard's theory of anesthesia has been substantiated again.

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VISCOSITY AND MOLECULAR WEIGHTS OF POLYMERIC MATERIALS*

BY ELMER O. KRAEMER AND FRANK J. VAN NATTA

The existence of an intimate relationship between the viscous behavior of colloidal solutions and their ultramicroscopic physical structure has long been acknowledged, but, with the exception of simple dilute suspensions to which Einstein's equation is applicable, it has not in general been possible to deduce quantitative conclusions concerning colloidal structure from viscosities. Although a number of different factors and conditions have been recognized as important—e.g., (1) aggregation, (2) electroviscous effects, (3) solvation, and (4) non-spherical particle-shape—the evaluation of the significance of each in a given case has usually been a matter of speculation. The influence of aggregation on viscosity has frequently been demonstrated by direct microscopic or ultramicroscopic examination of sols in which the particles are discernible and it is probably often significant also for the characteristic viscous behavior of lyophilic sols. Electroviscous effects, like electrokinetic phenomena in general, are restricted to conducting systems. Solvation has undoubtedly been over-emphasized in the past, for independent and, presumably, reasonably reliable estimations of the degree of solvation frequently fail to confirm the very high values deduced from viscosities. Although the effect of particle-shape should in special cases be calculable from hydrodynamic theory, no careful analysis was made until very recently. At our request Professor L. Onsager[1] has kindly worked out the case of a suspension of rotation-ellipsoids and has found that the shape factor of Einstein's equation (which is 2.5 for spheres of any size) increases with the square of the ratio of major to minor axes. The detailed calculations are, however, not yet available.

In the absence of a theoretical basis for taking particle-shape into consideration, efforts have been made to obtain empirical relations.[2] Of especial interest are the results of Staudinger and his associates for a number of natural and synthetic macromolecular substances, such as cellulose, rubber, and their derivatives, polystyrene, polyvinyl compounds, etc. These substances are typical, linear, high-molecular-weight polymers, and belong to the general

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* Communication No. 104 from the Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

[1] Washington meeting, American Physical Society, April 28-30, 1932; Physical Bulletin 7, No. 2, p. 7. By a less rigorous analysis, R. Eisenschitz: Z. physik. Chem., 158, 78 (1931), reached the conclusion that, as a first approximation, the shape factor in Einstein's equation increases linearly with the ratio of the major-to-minor axes of ellipsoidal particles.

[2] H. Staudinger: Kolloid-Z., 51, 74; 53, 19 (1930); 54, 129 (1931); Z. angew. Chem., 45, 276 (1932); Ber., 65, 267 (1932), and many earlier papers; H. Fikentscher and H. Mark: Kolloid-Z., 49, 135 (1929); H. Mark: 53, 32 (1930); H. Fikentscher: Cellulosechemie, 1932, 58.

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class of intrinsic colloids.[1] According to Staudinger, these substances pass into solution, in the absence of association, as single, rod-like molecules, and their high specific hydrodynamic volumes[2] are a consequence of the molecular form. For solutions of a given concentration and polymeric series, the viscosity was found to be proportional to the molecular weight (up to several thousand) and, therefore, to the length of the rod-like molecules. By extrapolation of empirical relationships established on low polymers, to which ordinary molecular-weight methods are applicable, Staudinger has estimated the molecular weights of many high polymers, including rubber and cellulose.

Since there are relatively few satisfactory general methods for determining the molecular weights of high polymers or for studying the nature of their solutions, Staudinger's conclusions are of great interest and his methods deserve careful examination. As a test of his methods, this paper presents results on a polymeric series of considerable range for which the molecular weights are believed to be known exceptionally accurately. It will be shown that Staudinger's equations only approximately describe the facts and must be used with caution. Molecular weights assigned by Staudinger to rubber, cellulose, cellulose derivatives, and very high polymers in general may be considerably in error, and are probably too high rather than too low, as he supposes.

Staudinger's Viscosity vs. Molecular-Weight Equations

Staudinger has employed two methods for calculating molecular weights from viscosity measurements on dilute solutions of the polymers.

Method I depends on the equation

$$(1) \quad \log \eta_r = K_{cm}Mc$$

where η_r is the relative viscosity compared to that of the solvent, K_{cm} is the "molecular weight-concentration constant"[3] and is specific to a given solvent and polymeric series, M is the molecular weight, and c is the concentration, which is usually expressed by Staudinger in terms of "base-molarity," i.e., the molarity of the recurrent group constituting the structural unit of the polymer. K_{cm} was evaluated from viscosity measurements on the lower members of the series, for which the molecular weights could be determined by the usual methods. The molecular weights of the higher polymers were then calculated from the viscosities of their solutions by extrapolation, using the above equation.

Method II depends on the equation

$$(2) \quad \eta_r - 1 = K_mMc$$

where K_m is a constant specific to the solvent and polymeric series. As Hess and Sakurada[4] have pointed out, this equation is not independent of equation

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[1] E. O. Kraemer and G. R. Sears: J. Rheology, **2**, 292 (1931).

[2] E. O. Kraemer and G. R. Sears: J. Rheology, **1**, 231 (1930).

[3] Staudinger, in effect, writes the constant of proportionality $1/K_{cm}$ instead of K_{cm}, but there is no apparent object in using the reciprocal form.

[4] K. Hess and I. Sakurada: Ber., **64**, 1183 (1931).

1, but is equivalent to the first two terms of the expansion of equation 1 when natural logarithms are used, K_{ir} being then equal to K_{em}. Equation 2 is to be used only at low concentrations where the relative viscosity is a linear function of concentration. It is in this respect equivalent to Einstein's equation, in which, however, K_mM is constant and equal to 2.5 when c is expressed as a volume fraction. *In this method also*, K_m is evaluated by *measurements* on members of the series with known molecular weights.

The Viscosities of Polymeric ω-Hydroxydecanoic Acids

For investigating the relation between viscosity and molecular weight more accurately than has hitherto been done, a series of polymers of the general formula $HO[(CH_2)_9COO]_xH$, formed by intermolecular esterification of ω-hydroxydecanoic acid, was selected because of the possibility of determining

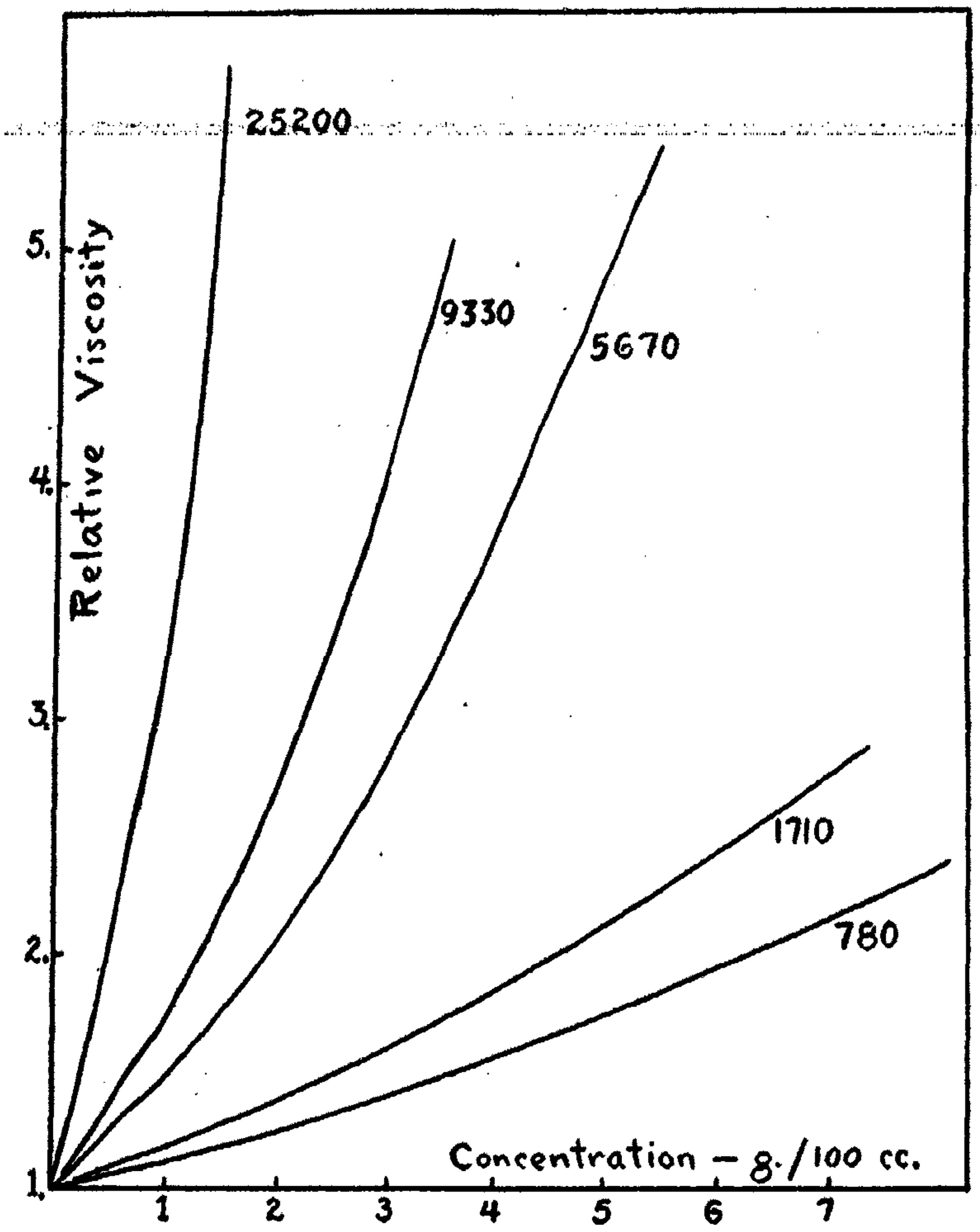

Fig. 1

Influence of Molecular Weight upon the Viscosity-Concentration Curves for Polymeric ω-Hydroxydecanoic Acids

TABLE I

Viscosity of Polymeric ω-Hydroxydecanoic Acid in *sym.*-Tetrachloroethane

		25°C.			50°C.	
Mol. Wt.	Wt. %	Density	g/100 c.c.	η_r	Density	η_r
780	0.2596	1.5816	0.4106	1.0449	1.5431	1.0370
	0.5174	1.5788	0.8169	1.0894	1.5408	1.0757
	1.747	1.5680	2.739	1.3583	1.5303	1.3015
	3.088	1.5559	4.804	1.7077	1.5185	1.5773
	5.158	1.5372	7.929	2.3536	1.5013	2.0896
1,710	0.1028	1.5826	0.1626	1.0245	1.5438	1.0223
	0.2532	1.5814	0.4004	1.0663	1.5423	1.0625
	1.311	1.5715	2.060	1.3950	1.5330	1.3414
	2.718	1.5588	4.236	1.9053	1.5210	1.7493
	4.591	1.5419	7.079	2.7949	1.5051	2.4606
5,670	0.1719	1.5820	0.272	1.1172	1.5432	1.1078
	0.3399	1.5805	0.5372	1.2409	1.5416	1.2196
	0.8568	1.5770	1.351	1.6425	1.5371	1.5951
	1.687	1.5697	2.647	2.5843	1.5313	2.3773
	3.436	1.5524	5.335	5.3302	1.5164	4.6341
9,330	0.05051	1.5832	0.07997	1.0495	1.5445	1.0458
	0.1025	1.5827	0.1622	1.1023	1.5438	1.0969
	0.4264	1.5797	0.6735	1.4772	1.5409	1.4337
	0.8598	1.5759	1.355	2.0759	1.5371	1.9657
	1.388	1.5711	2.181	3.0036	1.5327	2.7625
	2.228	1.5634	3.483	4.9055	1.5254	4.3871
16,900	0.02221	1.5837	0.03517	1.0357	1.5448	1.0333
	0.04434	1.5835	0.07021	1.0770	1.5447	1.0713
20,600	0.01589	1.5839	0.02516	1.0344	—	—
	0.03226	1.5836	0.05108	1.0670	—	—
25,200	0.01671	1.5838	0.02647	1.0452	1.5445	1.0418
	0,01717	1.5838	0.02720	1.0507	1.5445	1.0477
	0.04276	1.5835	0.06771	1.1233	1.5444	1.1143
	0.04365	1.5835	0.06912	1.1368	1.5444	1.1305
	0.08583	1.5831	0.1359	1.2497	1.5440	1.2317
	0.1709	1.5821	0.2703	1.5316	1.5431	1.4970
	0.3447	1.5806	0.5449	2.2208	1.5417	2.1210
	0.6026	1.5781	0.9508	3.2335	1.5393	3.0401
	0.9443	1.5754	1.488	5.7649	1.5373	5.2436

the molecular weights by titration of the terminal acid groups.[1] In this way higher molecular weights could be determined than by the customary physicochemical methods. The values so determined satisfactorily checked values obtained ebullioscopically on the lower members; the value for the highest

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[1] These polymers were prepared and fractionated by one of us (F.J.V.N.) in connection with polymerization researches with Dr. W. H. Carothers, and will be described in greater detail in a separate paper.

polymer was confirmed by ultracentrifugal analysis (titration, 25,200; centrifugal sedimentation equilibrium, 27,000).[1] Admittedly the polymers are not entirely homogeneous with respect to molecular weight. The ultracentrifugal analysis, for instance, indicated the presence of some material having a molecular weight above 27,000 and a small portion of smaller molecular weight. The uniformity was distinctly greater, however, than was expected, and was, we believe, probably quite as good as for the polymers of equal molecular weight that were used by Staudinger. Unfortunately, Staudinger gave no information concerning uniformity as definite as that obtainable with the ultracentrifuge.

The viscosities of dilute solutions in *sym.*-tetrachloroethane were accurately measured at 25 and 50° C. with a Bingham capillary viscometer. The results are presented in Table I and Fig. 1, and are discussed under the following topics.

Log Relative Viscosity vs. Molecular Weight (Staudinger's Method I)

The logarithms of the relative viscosities at 25° were plotted against the concentrations in grams per 100 cc. of solution. As usual for high-molecular-weight materials, the curves were in all cases concave to the concentration axis,[2] and, accordingly, could not be expressed by equation 1. The limiting slope at zero concentration therefore was determined for each curve (graphically), the values being given in Table II, column 2. In column 3 are given the values of K_{cm}, obtained from the values of column 2 by division by the molecular weight and multiplication by 17, the factor 17 being necessary to convert the concentrations to Staudinger's base-molar basis.

TABLE II

Mol. Wt.	$(\log \eta_r)/c_0$	$K_{cm} \times 10^4$*
780	0.0484	10.5
1710	0.0702	7.0
5670	0.173	5.2
9330	0.261	4.8
16900	0.452	4.5
20600	0.574	4.7
25200	0.778	5.2

* K_{cm} is defined by equation 1 when concentration is in terms of base-molarity, and corresponds to the reciprocal of Staudinger's K_{cm} constant.

According to Staudinger, K_{cm} should be a constant, characteristic of a particular polymeric series and solvent. The values given in Table II suggest that K_{cm} reaches a constant value of about 5×10^{-4} near a molecular weight of 5,000, on the basis of which the higher molecular weights might be roughly calculated by equation 1.

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[1] We are indebted to Dr. W. D. Lansing of this laboratory for the ultracentrifugal analysis.

[2] J. W. McBain, C. E. Harvey and L. E. Smith: J. Phys. Chem., 30, 312 (1926); H. Fikentscher: Cellulosechemie, 1932, 58.

As a matter of fact, however, the variation in K_{em} above a molecular weight of 5,000 distinctly exceeds the experimental error, and the calculation of K_{em} simply confuses the actual relationship between viscosity and molecular weight. This becomes evident when $(\log \eta_r)/c_o$ is plotted against molecular weight. The curve is indeed practically linear for molecular weights below 17,000, but it does not extrapolate through the origin, as required by equation 1. For molecular weights exceeding 17,000, an upward curvature becomes detectable, i.e., $(\log \eta_r)/c_o$ gradually increases more rapidly than the molecular weight. If the curvature continues with increasing molecular weight, as seems likely, the discrepancy between the actual viscosity and the viscosity calculated from equation 1 becomes greater with increasing molecular weight.

Since there is greater theoretical justification for using a linear equation relating viscosity and concentration (equation 2), and since, as pointed out above, equations 1 and 2 are essentially identical for low concentrations, a more detailed discussion of the results is left for the following section.

Relative Viscosity vs. Molecular Weight (Staudinger's Method II)

The influence of particle shape and structure on viscosity is most simply revealed at very low concentrations, where mutual interference of the particles is negligible. Under these conditions, the relative increase in viscosity over that of the solvent is directly proportional to the concentration.

The relative viscosities for the lowest concentrations (Table I) were plotted against concentration on a large scale. Although a slight departure from linearity could be detected for the highest polymers, rather accurate values for the slopes at zero concentration ($= (\eta_r - 1)/c_o$) could be obtained. This quantity may be termed the "specific increase in relative viscosity," and its values are given in Table III, column 2 (for 25°) and column 3 (for 50°C.), c being expressed in grams of solute per 100 cc. of solution. According to equation 2, the ratios of these slopes to the corresponding molecular weights should be constant, as well as the K_m values (column 4), obtained by multiplying these ratios by 17 (a base-molar solution of hydroxydecanoic acid polymer containing 17 g./100 cc.). The K_m-values are directly comparable to Staudinger's K_m-values. The average of the ratios of corresponding K_m's and K_{em}'s is 2.37, instead of 2.30 as required theoretically by the relationship between equations 1 and 2 when Briggsian logarithms are used in connection with equation 1.

Table III

Mol. Wt.	$(\eta_r-1)/c_o$ (for 25°)	$(\eta_r-1)/c_o$ (for 50°)	$K_m \times 10^4$ (25°C.)
780	0.109	0.093	23.7
1710	0.157	0.145	15.6
5670	0.425	0.403	12.7
9330	0.615	0.586	11.2
16900	1.04	1.00	10.5
20600	1.32	—	10.9
25200	1.84	1.75	12.4

The K_m-values show a systematic drift like that of the K_{cm}-values of Table II. A similar drift is evident in Staudinger's data for polyvinyl acetate,[1] polystyrene,[2] and cellulose acetate.[3] With the highest hydroxydecanoic acid polymers an approximately constant value of 12×10^{-4} appears to be attained, which is the same as that found by Staudinger[4] for cellulose and cellulose acetate, but distinctly larger than the values for paraffin hydrocarbons (0.85×10^{-4}), polystyrenes (1.8×10^{-4}), rubber and hydrorubber (3×10^{-4}), polyoxymethylenes (2.2×10^{-4}), and polyvinyl acetates (3×10^{-4}). As Staudinger has shown, the differences in the K_m's for different polymeric series are to a first approximation related in a simple way to the length of the recurring unit in the polymeric chain. Specifically, when n is the number of atoms per recurring unit in the polymeric chain, the ratio K_m/n is approximately constant; i.e., $K_m/n = K_{eqv}$. To the extent that equation 2 is applicable, this means that the relationship between viscosity and molecular weight is the same for different polymeric series when concentrations are expressed in terms of molarity of chain-atoms (i.e., nc). For the case of the hydroxydecanoic acid polymers, n equals 11, and K_{eqv} equals 1.1×10^{-4}. This is thus not greatly different from the values found by Staudinger for hydrocarbons in tetralin or benzene (0.85×10^{-4}), hydrocarbons in carbon tetrachloride (1.14×10^{-4}), polyoxymethylene in chloroform (1.1×10^{-4}), cellulose in cuprammonium and cellulose acetate in *m*-cresol (2.4×10^{-4}).

On the whole, therefore, the hydroxydecanoic acid polymers show the same relations between viscosity and molecular weight as Staudinger has described for other linear polymers of low and intermediate molecular weight (up to about 10,000). However, the applicability of these relations by extrapolation to the estimation of the molecular weights of high polymers is a matter requiring closer scrutiny of the data for its justification. Two principal points are involved: the accuracy with which the relationship between viscosity and molecular weight is known over the range of molecular weights that can be measured by reliable methods, and the probability that the empirical relationship holds far outside the range in which it is experimentally established.

With respect to the first point, reference was made above to the approximate constancy of K_m for molecular weights above 5000. As a matter of fact, however, the inconstancy of K_m is definitely greater than the experimental error, and equation 2 does not accurately represent the facts. The relation between $(\eta_r - 1)/c_0$ and molecular weight is more adequately shown graphically (Fig. 2), whereupon it is evident that the relation is indeed a linear one over a rather wide range of molecular weight, but not one of simple proportionality. Whereas the inconstancy of K_m would suggest an anomalous situation at low molecular weights, the curve reveals no such thing. The significance of the marked variation in K_m at low molecular weights and of the attainment of

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[1] Ann., 488, 16 (1931).

[2] Ber., 63, 222 (1930).

[3] Ber., 63, 3132 (1930).

[4] Ber., 65, 267 (1932).

approximate constancy at higher molecular weights is obvious. Up to molecular weights of about 17,000, the curve is represented by the equation[1]

$$(3) \qquad (\eta_r - 1)/c = 0.065 + 5.85 \times 10^{-5} M$$

when concentrations are in grams per 100 cc.

Above 17,000, however, a distinct upward curvature becomes evident, and equation 3 also fails to be applicable. The calculation of molecular weights of hydroxydecanoic acid polymers in the range of 100,000 or higher by equations 2 or 3 from viscosity data would obviously give quite erroneous results. The selection of a non-linear empirical equation for use in extensive extrapolations would be too arbitrary to be useful in a case of this sort.

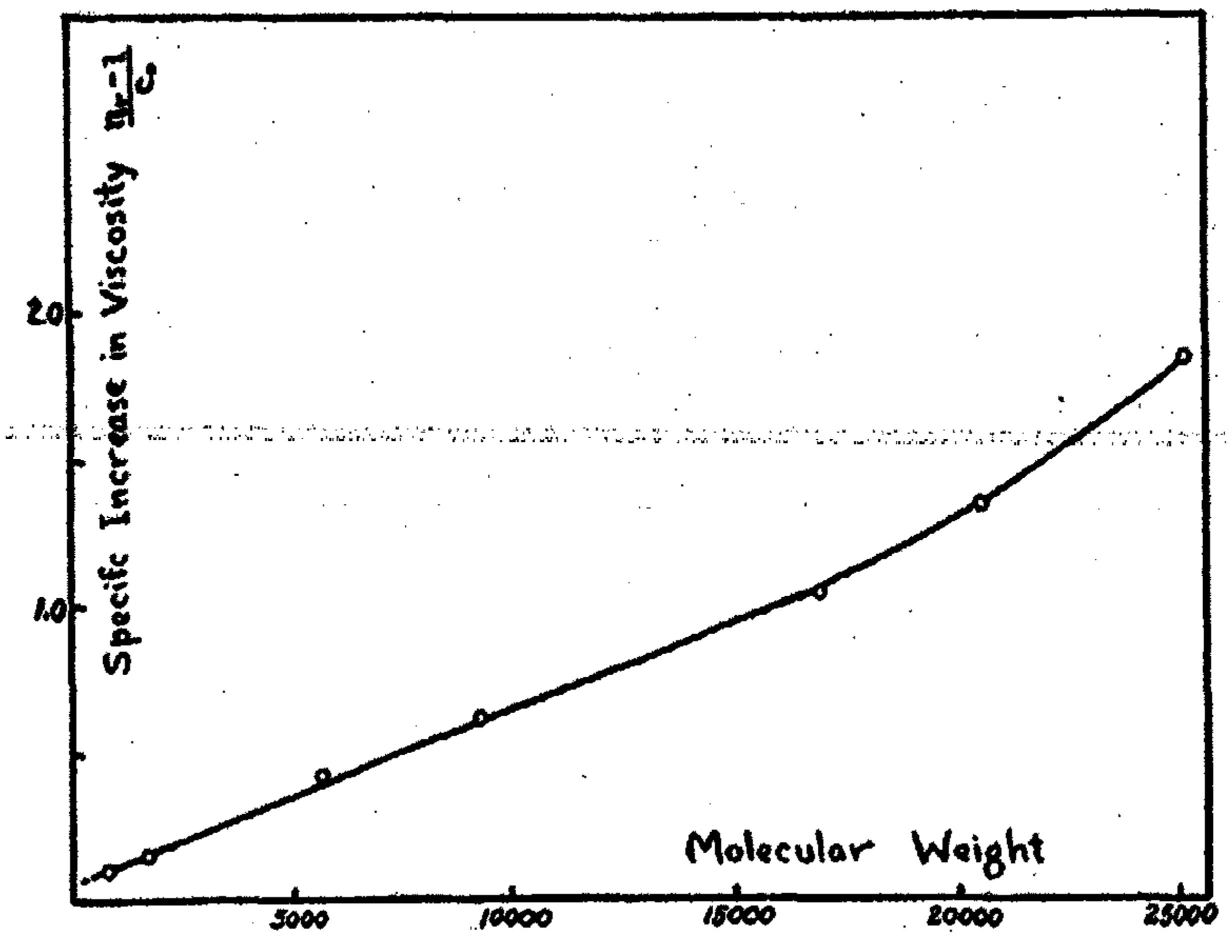

Fig. 2

Specific Increase in Viscosity vs. Molecular Weight for ω-Hydroxydecanoic Acid Polymers

Whether the results presented here should be considered typical of linear polymers, it is not possible to say with definiteness, but there is no apparent a priori reason why they should be considered exceptional. It is true that Staudinger and his associates have not described similar results. In most cases, however, Staudinger's molecular weights, determined cryoscopically, become decidedly unreliable above 10,000 (for which freezing-point depressions of less than 0.01° were measured) and values of K_m were usually calculated from data below 15,000. It seems possible, therefore, that the linear relationship shown below 15,000 would break down at higher molecular weights for some of the polymeric series studied by Staudinger as well as for the hydroxy-

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[1] Equation 3 is identical in type with that used by Staudinger and Ochiai: Z. physik. Chem., 158, 35 (1931), in taking account of the effect of end groups.

decanoic acid series. Although the departure from linearity might not take the form of an upward curvature as in Fig 2, it would in general seem desirable to admit the possibility of departure from linearity at high molecular weights unless definite evidence to the contrary was available. Linear relations over very wide ranges of the variables involved are after all rather exceptional. It is interesting and suggestive to carry out calculations involving wide extrapolations, but it seems to us unfortunate and almost without precedent to assert definitely and positively, as Staudinger does, without any theoretical and very little experimental support, that a linear relation established between molecular weights of 0 and 15,000 must hold in the range of 150,000 and over. While granting that Staudinger's calculations indicate that rubber, cellulose, their derivatives, and certain synthetic polymers like polystyrene have very high molecular weights, we consider the numerical values as possibly a good deal in error, and probably too high.

Fikentscher's Equation

Fikentscher (loc. cit.) has recently proposed an equation containing a single arbitrary constant, which, although empirical, appears to be superior in general applicability to any hitherto used: namely

$$(4) \qquad \log \eta_r = \frac{75\, k^2 c}{1 + 1.5 kc} + kc$$

where c is the concentration in grams per 100 cc of solution and k is the arbitrary constant, which Fikentscher calls the "eigenviskosität."

In order to determine the relationship between k and molecular weight, the k's were calculated for the hydroxydecanoic acid polymers. Suitably rearranging equation 4 and setting $c = 0$ gives $\log \eta_r/c_0 = 75\, k^2 + k$, with which the values of k may be conveniently calculated from the values of $(\log \eta_r)/c_0$ given in Table II. The k's are given in Table IV, column 2. The curve of k against molecular weight is concave to the molecular weight axis and rather strongly curved. It consequently does not provide a satisfactory substitute for equations 2 and 3 for determining the molecular weights of high polymers by extrapolation.

In passing, attention may be called to columns 4 and 5 illustrating the success with which Fikentscher's equation reproduces the observations on the hydroxydecanoic acids. When k is selected to fit the viscosities of dilute solutions, as in the present case, the calculated viscosities for more concentrated solutions may differ considerably from the observed values. The discrepancies are not so glaring if the constant k is calculated from the viscosities of the concentrated solutions. For instance, the calculated and observed viscosities for the low concentrations of the highest polymer agree to about 5 per cent when k is calculated from the data on the most concentrated solution. It is of interest to note that the k for the highest hydroxydecanoic acid polymer is about equal to the k's found by Fikentscher for "medium viscosity" nitrocellulose in acetone and for rayon in cuprammonium.

TABLE IV

Mol. Wt.	k	Concn.	Obs. η_r	Calc. η_r
780	0.020	7.929	2.35	2.19
1710	0.025	7.079	2.79	2.68
5670	0.042	5.335	5.33	5.58
9330	0.058	3.483	4.91	5.66
16900	0.071	—	—	—
20600	0.081	—	—	—
25200	0.0954	0.1	1.19	1.19
		0.5	2.05	2.32
		1.0	3.42	4.93
		1.5	5.85	9.68

Temperature Coefficient of Viscosity

An important argument in support of the view that the unit in solutions of linear polymers is the single unsolvated molecule is provided by the fact that the relative viscosity is affected but slightly by changes in temperature. As may be seen in Table V, the ratio of $(\eta_r - 1)/c_0$ at 25° and 50° is practically constant for all except the lowest polymer and differs but little from unity. The departure from unity may be due to a small solvation effect.

TABLE V

Mol. Wt.	780	1710	5670	9330	16900	25200
Temp. Coeff.	1.17	1.08	1.05	1.05	1.04	1.05

Effect of Rate of Shear

A characteristic feature of the viscosity of solutions of high polymers, particularly those with a large specific hydrodynamic volume, is their failure to show a constant viscosity at different rates of shear. In general, the variation in viscosity with rate of shear increases with the concentration and the specific hydrodynamic volume. As the concentration is reduced, the magnitude of the effect may become too small to detect, but it probably does not completely disappear. For the highest concentrations of the highest polymer used in this investigation, an increase in pressure from 97 to 530 g./cm.^{2} caused a drop in viscosity of about 3%. In other cases, the effect was less, and could be disregarded for the purposes of this investigation. It is not to be denied, however, that this is a significant property of macromolecular solutions.

Experimental Details

Preparation of Materials: The polymeric ω-hydroxydecanoic acids were prepared by heating the monomer at various temperatures and pressures for different times, depending upon the degree of polymerization desired. The polymers were fractionally crystallized to increase the homogeneity. The molecular weights were determined by titration of chloroform-alcohol solutions of the polymers with alcoholic potassium hydroxide.

The tetrachloroethane was washed with water, dried and redistilled. It was characterized by the following properties: boiling range, 143.5-144° at 76 cm; density $^{25}_{4}$ = 1.5842; N_D^{25} = 1.4920; absolute viscosity at 25° = 0.01610 poises. Its viscosity remained unchanged during the course of the investigation.

The solutions were made up by weight and the densities were determined pycnometrically. Since a detectable decrease in viscosity of the solutions, *especially of the higher polymers, occurs during a few days, the viscosities* were measured on fresh solutions.

Viscometry: The viscosities were measured in accordance with Bingham's procedure for accurate viscometry.[1] The viscometer was of the standard Bingham type and had the following dimensions: capillary length, 9.85 cm.; average effective radius (calculated from the efflux time for the standardizing liquid), 0.01512 cm.; efflux volume, 3.963 cc. The construction of the viscometer was reasonably symmetrical, the efflux times for the two directions of flow differing by but a fraction of a percent. The two times were therefore averaged.

The constants of the instrument were determined by calibration with gas-free water at 25° and 50°C. The kinetic-energy instrument constant was obtained from the variation of efflux time with pressure by Knibb's method (see Bingham's book). In the equation $\eta = cpt - c'd/t$, $c = 5.206 \times 10^{-7}$ and $c' = 0.0309$. The kinetic energy correction rarely amounted to 1% of the total pressure for measurements at 25° and seldom exceeded 2% at 50°.

The efflux times were measured with two checked 0.1-second stop watches. The time was never less than 150 seconds at 25° or 100 seconds at 50°, and usually was considerably greater.

The pressures were read on mercury or dibutyl phthalate manometers, depending on the magnitude of the pressure, with a steel tape graduated in millimeters. The difference in level was never less than 12 cm. and was usually considerably greater. The customary corrections were applied for expansion of the tape, buoyancy, etc.

The temperatures of the two thermostats used were held at 25° ± 0.03 and 50° ± 0.03, as determined by a thermometer with Bur. Stand. certificate. After determination of the mean efflux time at 25°, the viscometer was transferred to the 50° thermostat without refilling, the volume was readjusted, and effluxes at 50° observed. Occasionally, the viscometer was again returned to the 25° bath to assure reversibility.

During filling of the viscometer, the solutions were filtered through a sintered glass disc under conditions effectively preventing evaporation of solvent or contamination from the air. Evaporation was also guarded against while the efflux times were being determined.

In general, the inconsistency of the results was less than 0.2%.

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[1] E. C. Bingham: "Fluidity and Plasticity" (1922).

Summary

Careful measurements of the viscosities of solutions of polymeric hydroxydecanoic acids with molecular weights from 780 to 25200 inclusive show that a simple relationship exists between viscosity and molecular weight over a wide range of the latter, in qualitative agreement with observations of Staudinger for numerous polymeric series. The quantitative expression of the relationship, however, requires a modification of the Staudinger equation. In the range of high molecular weights (above 15,000) the simple relationship breaks down for the polymeric ω-hydroxydecanoic acids. In the light of these results, Staudinger's values for the molecular weights of rubber, cellulose, and other very high polymers are unreliable.

ADSORPTION OF OXALIC ACID BY ALUMINA

BY PHILLIP H. DEWEY

When studying the oxidation of acetaldehyde by hydrogen peroxide in presence of an alumina catalyst made from aluminum nitrate, there was an apparent loss of acetaldehyde. Since acetic acid and oxalic acid are the two most probable oxidation products, some experiments were made with acetic acid and oxalic acid to determine whether there was any difficulty in analyzing for them in presence of alumina. Acetic acid can be washed out of the alumina without difficulty and titrated with alkali. This is not possible with oxalic acid. A solution containing 20 g Al_2O_3, 100 cc H_2O and 0.36 g oxalic acid was allowed to stand for six days and was then extracted for twenty-seven hours in a Soxhlet apparatus. Titration showed 0.0153 g oxalic acid, less than five percent of what should have been found.

This might have been due to the formation of an insoluble oxalate or to very strong adsorption. Runs were therefore made with acetic acid and with oxalic acid. The results are shown graphically in Fig. 1. It is clear that no compound is formed in either case and that oxalic acid is adsorbed very strongly at the low concentrations. At the higher concentrations there is enough alumina peptized to give an almost gelatinous precipitate when neutralized with caustic soda. In cases where the precipitate is at all marked, the determination of the oxalic acid in solution gives low results when titrating with alkali, using phenolphthalein as an indicator. The end-point is indefinite, the first pink appearing at a value as much as forty percent low in the case of a 0.015 M solution. If the titrations are made hot and alkali enough is added to give a permanent pink when boiled for two minutes, the proper value is obtained.

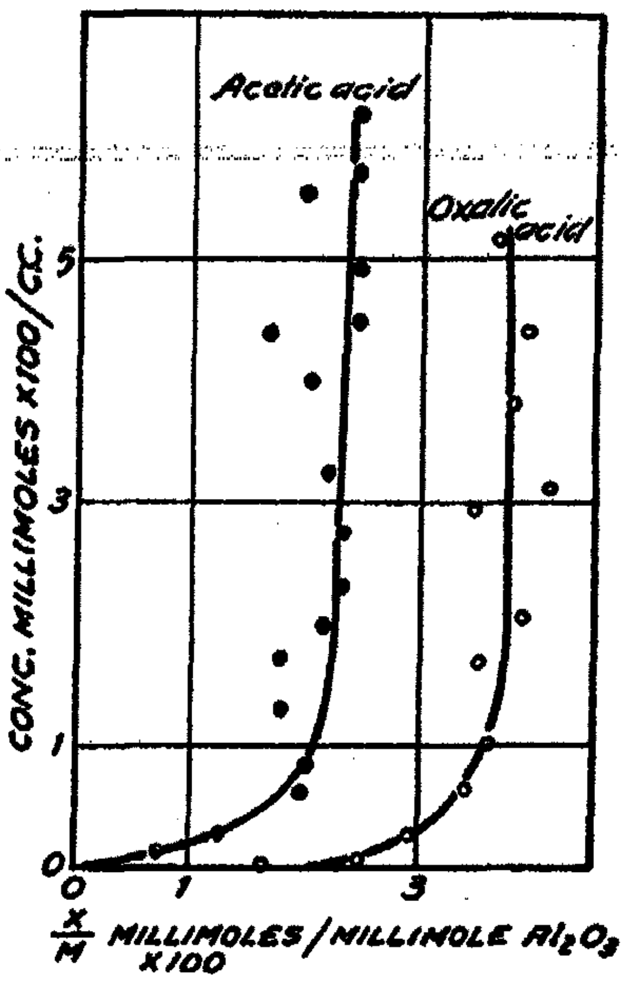

FIG. 1

Adsorption Curves for Oxalic and Acetic Acids

● Curve II Acetic Acid

○ Curve I Oxalic Acid

It is possible to determine the free and adsorbed oxalic acid with the regular hot acid permanganate titration.

Summary

1. Acetic acid and oxalic acid form no compounds with an alumina catalyst at room temperature.

2. Oxalic acid is adsorbed much more strongly than acetic acid by an alumina catalyst.

3. Oxalic acid cannot be washed out of alumina in any reasonable time.

4. Oxalic acid adsorbed by alumina can be determined satisfactorily by the hot acid permanganate titration.

This work was done under the direction of Professor Bancroft.

Cornell University.

A MODIFIED ELECTRO ULTRAFILTER

BY D. VON KLOBUSITZKY

The electro ultrafilter of Bechhold,[1] which, as is known, gives a rapid dialysis, at the same time concentrating the solution, is for that reason of the greatest utility in the laboratory for chemical and physical chemistry purposes, but it has for us the inconvenience of being made with an apparatus of porcelain Bechhold-König only manufactured in Germany. This makes it necessary to buy spare parts or in the case of breakages to interrupt the work for some time. The first alternative is very expensive and the second retards the work. My end therefore was to construct an electro ultrafilter with easy mounted parts in common use.

For model I used a large Bechhold electro ultrafilter with suction in only one direction. As a recipient for the solution I used a strong glass cylinder having at one of its extremities a neck. This recipient was closed with a membrane of parchment tied with a thread to stop the entrance of water (when it was necessary I waxed or covered the outer side of the parchment with a layer of a liquefied mixture of wax and colophony). In this recipient was placed a porcelain candle of any make. This candle was completely glazed with the exception of the bottom and closed with a rubber stopper containing two bores, to one of which was connected an electrode of platinum which went to the bottom and to the other a glass tube in the form of an L reaching also to the bottom. The wall at the bottom of the candle was, as in the Bechhold-König recipient, in the first place placed in a solution of 10% collodion in acetic acid and afterwards hardened and washed in water until all traces of acetic acid had disappeared. Thus the two recipients remained impermeable to colloids.

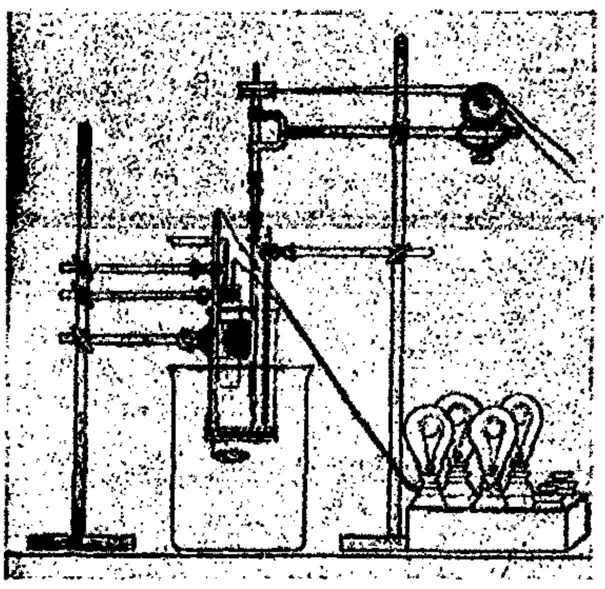

FIG. 1

Below the parchment membrane was placed an electrode of silver: in the glass recipient an agitator and thermometer: all the apparatus was remaining in a vessel containing distilled water. A continual current of the maximum 110 volts and 0.5 amperes was connected: the positive pole to the interval platinum electrode and the negative pole to the end of the silver electrode. A tube in the form of an L was connected to a tap of water. The reaction of the solution dialysed could be regulated by the intensity of the suction.

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[1] H. Bechhold: Z. physik. Chem., 60, 257 (1907).

When the colloid solution contained a large quantity of electrolytes it was necessary to augment the distance of the silver electrode from the parchment membrane to avoid warming and so coagulating.

With regards to the remaining characteristics the method of dialysing and the functional capacities were equal to the apparatus of Bechhold.

The mounting of the apparatus can be seen from the sketch, Fig. 1.

Summary

An article on an apparatus for an electro ultrafilter easily mounted and for common use.

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NEW BOOKS

Liesegang Rings and Other Periodic Structures. *By Ernest S. Hedges. 22 × 15 cm: pp. viii + 122. London: Chapman and Hall, 1932. Price:1 10 shillings, 6 pence.* Well-known monographs on the above subject have been published by Liesegang, E. Küster and others, and there have been sections devoted to it in the textbooks of colloidal chemistry. *This is the first book on the subject written in the English language.*

The very considerable interest that has been aroused in the subject among chemists and also among biologists and botanists can be clearly traced in the complete bibliography that is included by Dr. Hedges in this volume. This ranges from 1896, when the first paper was published by Liesegang, up to the present date. This bibliography alone will prove of the greatest service to all interested, and especially to those wishing to carry out original research on some aspect of this subject.

Dr. Hedges has a first chapter giving a brief account of those aspects of colloidal chemistry a knowledge of which is necessary for a comprehension of the later chapters of the book. He gives an account of the main experimental facts under such headings as, influence of various conditions, variations of structure, chemical analysis of structure, etc. There is *included an interesting account of periodic structures produced in capillaries from the inter*action of both gases and liquids and of periodic diffusion structures produced without chemical reaction. There is a chapter on periodic structures obtained on crystallisation, evaporation, condensation, sedimentation, etc., and a short but very interesting account of natural periodic structures.

A comprehensive and critical treatment is given of the many theories that have been put forward to account for these phenomena. To many this section of the book will be considered its most valuable feature; the literature on this subject has become so bulky, 270 papers having been published in the last ten years, and the experimentation is frequently of such a character, that it is difficult to correctly appreciate the true scientific implication of the results. In the opinion of the reviewer anyone reading this delightful book of Dr. Hedges will conclude that *we are very far yet from any comprehensive theory which is more than quali*tative in character. There is therefore a very definite need now for this book which should stimulate research in the direction of a mathematical theory.

The book is well printed and there are some beautiful illustrations.

D. C. Jones

A Short Course in Qualitative Analysis. *By F. E. Brown. 20 × 13 cm; pp. xiii + 332. New York City: The Century Company, 1932. Price $2.25.* Another text on Qualitative Analysis has been added to the long list of those already published within the last five or ten years. Very little in the way of new methods has been presented, and such a text would be uncalled for if it were not for the fact that each instructor must teach Qualitative Analysis with the aim in view of adapting his course *to the students' previous training in chemistry.*

This book has been developed from the author's mimeographed notes used, with revision from time to time, by approximately 3000 students. It is without doubt admirably suited for large classes of students who have not had a full year of beginning chemistry. The course as outlined is planned for a quarter of eleven weeks, following two quarters of General Chemistry. The experimental part of the course requires about sixty hours of actual laboratory work and should be accompanied by two lectures or recitation periods per week.

Part I, Theory, includes 146 pages and is divided into ten chapters as follows: Solutions, Ionization, Reversible Reactions and Equilibrium, Mass Law and Solubility Product, Hydrolysis, Oxidation and Reduction, Types of Reactions and the Writing of Equations, Amphoteric Hydroxides, Complex Ions, The Colloidal Condition. This part of the text is well written and contains enough theory for a thorough understanding of the *analytical* procedure. Several sections are devoted to the development and explanation of the Mass

Action equation and its corollary the Solubility Product equation. In addition the Solubility Product equation is developed mathematically from the standpoint of Ionization from Crystals. The author gives two general types of chemical reactions, one in which no change of valence takes place and the other involving valence change. These general types are further divided into nine subdivisions. Numerous questions and problems conclude each chapter in this section. They cover thoroughly the important parts of the chapter and should give the student a fair idea of what he is expected to know.

The second part of the text, comprising 65 pages, is devoted to Preliminary Experiments on the basic and acidic radicals. They involve the actual separations and tests which are used later in the scheme of analysis. These simple experiments with questions related to them should enable the student to analyze an unknown substance intelligently and correctly.

Part III deals with the ordinary scheme of analysis for the usual cations and anions. This scheme is so arranged as to make the tests as fool-proof as possible and to eliminate all unusual and expensive apparatus, dangerous chemicals, etc. The author states that he has omitted fusions since they are unsatifactory in porcelain crucibles and nickel or platinum is too expensive to use with large classes. Therefore no test for silicates is included.

The appendix contains a table listing the ordinary properties of the common inorganic compounds for each cation studied in the course. In addition it contains directions for preparing reagents, test solutions, etc.

Throughout the text the author has succeeded beyond our expectations in bringing together theory and practice. It appears that his aim has been, as it should be in any short course, to stress a complete understanding of what is being done rather than the actual performance of the task. He has given extended illustrations of the theory which might seem unnecessary to the instructor but which are exceedingly valuable to a freshman. However, in certain sections he appears to be inconsistent. After explaining the Mass Action and Solubility Product equations, on page 85 he proceeds to write $C_{H^+} \times C_{OH^-} = K_{s.p.}$ We ordinarily think of the Solubility Product equation as being applied to saturated solutions of slightly soluble substances. The chapters on Oxidation and Reduction and the Writing of Equations would be more appropriate near the beginning of the book. Many students know little or nothing about writing equations when they start Qualitative Analysis. The sooner they learn it the better.

The procedure used for the analysis of the alkaline earth group has proven unsatisfactory in the experience of the reviewer. Complete precipitation of barium as chromate cannot be made in acetic acid solution without the addition of an alkali acetate. Flame tests are used for final identifications here as well as in the tests for sodium and potassium. Flame tests are unsatisfactory in the hands of beginning students, especially when the separations are somewhat incomplete. The alkaline earth metals may be separated and identified, without resort to flame tests, if the proper precautions regarding concentrations, digestion, and general manipulation are observed. The use of paranitro-benzeneazoresorcinol in the test for magnesium is a decided improvement over the classical magnesium ammonium phosphate test.

A few typographical errors appear throughout the book. The first sentence in the introduction fails to make sense. On page 16 the formula of sodium sulphate is written $NaSO_4$, so consequently the equation is unbalanced.

The book as a whole is a valuable addition to our Qualitative Analysis texts, and many instructors should find it well adapted to the courses which they teach.

Alfred W. Avens

Elektrolyte. *By Hans Falkenhagen. 25×18 cm; pp. xvi+346. Leipzig: S. Hirzel, 1932. Price: 23 mark unbound; 24.8 marks bound.* The rapid development in the theory of electrolytes which has followed the mathematical investigations of Debye and Hückel has given rise to an extensive literature which is distributed through many journals in different languages. The importance of the subject has made the need of a comprehensive survey of the whole field obvious to all physical chemists, and it is therefore very satisfactory that Prof. Falkenhagen, who has made important contributions to the study of electrolytes, should have brought together so much material in a compact, uniform, and systematic treatise. The classical theory is treated briefly yet adequately, in particular the thermodynamic foundations and equations required in the development of the new theory are deduced, and a uniform system of notation is a considerable aid to the comprehension of the subject. The theory of activity is then dealt with in a very clear and sufficient manner, and on page 74 the reader is fully prepared to begin the study of the behaviour of strong electrolytes. A good account of the effects of field strength and frequency on the conductivity of electrolytes provides an experimental foundation for the fundamental conception of interionic forces. It appears that an effect not taken into account by the theory of Debye and Hückel may make itself felt with high field strengths, viz., the ionisation by collision which formed the basis of the explanation offered by Larmor and by the reviewer many years ago for the anomalies of strong electrolytes. Although this effect is not adequate to account for the deviations with ordinary field strengths, it seems as if it must be taken into account in a complete theory of conductivity. The theory of strong electrolytes, both from the point of view of thermodynamics and also of conductivity, follows. In this part the mathematical treatment is full and clear, although a few misprints are troublesome and it is sometimes difficult to trace the origin of equations used owing to neglect of cross references in a few cases. Where so much care has been taken to make the whole intelligible it is a pity that in a few cases the thread has been lost in this way. The section on conductivity is more difficult, partly on account of the inherent difficulty of the subject and partly by the use of vector notation where it is not necessary. The very general development of this part of the subject, which cannot be followed up in detail, is no doubt valuable from the point of view of the mathematician, but the chemist will miss here what he might have been led to expect from the earlier part of the book, that is, a gradual development of the theory from the simple case, which is after all nearly all the theory is competent to attack at present, to the more general treatment.

The extensions of the Debye-Hückel theory to more concentrated solutions made by Hückel, Bjerrum, Gronwall, LaMer and Sandved, are dealt with in a very satisfactory manner and the evidence of incomplete ionisation is also fully considered. This part of the book is especially valuable. The book closes with an account of the method of statistical mechanics due to Fowler, in which some misprints may offer difficulty to some readers. This method, although superficially more general than that of Debye and Hückel, is really not so, since the Boltzmann and Poisson equations both appear in it. It is interesting exercise in elementary mathematics but goes no deeper than the usual method.

This book gives a comprehensive and authoritative survey of the theory of strong electrolytes, including recent experimental researches, and may be recommended to physical chemists. It goes much further than any other collected accounts which have appeared, and brings the whole subject up to the modern standpoint.

J. R. Partington

Lehrbuch der physikalischen Chemie. *By Karl Jellinek. Vol. IV, Part 2. 25 × 17 cm; pp. 289-624. Stuttgart: Ferdinand Enke, 1932. Price: 30 marks.* The comprehensive treatise of Jellinek is planned to fill five volumes, of which three have been published complete and part of the fourth has appeared. It is an excellent work, carefully planned, clearly and accurately written, and comprising not only what is probably the best account of the theory of the subject which has yet appeared but also a wealth of numerical data and description of experimental methods which makes it invaluable in the laboratory. The general plan resembles that of Ostwald's famous *Lehrbuch*, of which it may be considered the modern successor. The present publication forms the second installment of the fourth volume and begins and ends with an incomplete sentence. The first 17 pages complete the section on electrolytic equilibria of the preceding issue and the rest deals with the theory of concentrated mixtures (solutions). This is divided into three parts, the first (53 pages) dealing with gas mixtures, the second (267 pages) with liquid mixtures, and the third (half a page at the end) beginning the treatment of mixed crystals. The first two sections are complete.

They deal with equations of state, thermal magnitudes and thermodynamics, chemical equilibria and electro-chemistry, including fused salts. As in other parts of the work, the mathematical parts are very clear and the equations derived are capable of direct experimental application. The experimental methods are fully described and the apparatus figured, and the numerical results are collected and tabulated. The references to the literature are numerous, and include American work. The volume is a welcome contribution to the literature of physical chemistry and should be in every chemical library.

J. R. Partington

Über eine neue Klasse von Verbindungen des positiv einwertigen Jods. *By Heinrich Carlsohn. 24 × 16 cm; pp. iv + 63. Leipzig: S. Hirzel, 1932. Price: 2.50 marks.* In this monograph the author describes the preparation and properties of a new class of complex compounds in which electropositive univalent iodine stabilised by coordination with pyridine functions as a salt forming radical.

Two types of these iodine coordination compounds are recorded, in one of which the iodine is coordinated with two molecular proportions of pyridine and in the other with one molecular proportion of this base. The former complex, which is the less stable, is produced by the action of iodine on a solution of an argentous or mercurous salt in the presence of pyridine.

$$[Ag.2py]\,NO_3 + I_2 = [I.2py]\,NO_3 + AgI$$

In addition to the foregoing nitrate salts of this dypyridino-iodine complex have been obtained with other strongly electronegative anions such as the perchlorate, sulphate and hydrogen sulphate.

Derivatives of the more stable monopyridino-iodine complex are formed by the action of iodine or argentous salts of organic acids in presence of pyridine.

$$[Ag.pyX] + I_2 = [I.py.X] + AgI$$

In these complexes X represents such acidic radicals as the acetate, benzoate, nitrobenzoate and benzilate. Similar compounds are described with dibasic acidic radicals, for instance, the oxalate, succinate and phthalate. A chloride and a bromide of this series are also indicated.

The physical properties of these complex iodine derivatives have been closely studied including solubility in organic solvents and electrical conductivity measurements which support the structural formulae, [I.2py] X and [I.pyX] for the two types each involving a coordination number of two for the pyridino-iodine complexes.

When a solution of the nitrate $[I.2py]NO_3$ is electrolysed the iodine is liberated exclusively at the kathode and this decomposition in conjunction with the fact that many metals displace iodine from these complex salts reveals the electropositive character of the iodine atom.

Considerable space (pp. 9-15) is devoted to analytical methods and a new gravimetric estimation of pyridine as the salt $[Cr(CNS)_4.2NH_3]H.py.\frac{1}{2}H_2O$ of Reineck's acid is described.

The results might, however, have been described more concisely and analytical details should preferably have been summarised in a short appendix. *G. T. Morgan*

Tables of Cubic Crystal Structure of Elements and Compounds. *By I. E. Knaggs, B. Karlik and C. F. Elam. 25 × 16 cm; pp. 90 + blank pages for notes. London: Adam Hilger, Ltd., 1932. Price: 11 shillings, 6 pence.* Roughly twenty years have elapsed since W. L. Bragg's pioneer work indicated the atomic arrangement in the cubic crystals NaCl and KCl. Since then the subject has grown enormously, becoming at once a new branch of physics, chemistry and mineralogy with a large literature of its own. The efficiency of the research worker is very much increased if there is available a reliable handbook summarising the results of previous work. The present summary of cubic crystal structure by Drs. Knaggs, Karlik and Elam, although admittedly not a rival, follows closely on the much more comprehensive "Strukturbericht" of Ewald and Hermann and should prove useful to those who have not access to this work. The book is divided into two parts, the first of which sets out the chemical formulae of the inorganic and organic substances dealt with and gives key numbers to further tables containing structure details, and full bibliographical references. Part II, contributed by Miss Elam, is a valuable summary of work on alloys belonging to the cubic system. A useful feature is the arrangement of crystal structures in order of lattice spacing. The lists of references are complete up to August 1931 and the tables are well printed on good paper. Considering the limited scope of the work, its price seems rather high.

The letter P, used extensively throughout the tables as a lattice symbol, appears to be confused with the letter S of the explanatory introduction. A fuller use of the new nomenclature enabling characteristic co-ordinates of atoms in the more complicated cells to be read off would have added to the value of the tables. A minor error is the use of Wo for W on page 80 and authors' initials are incorrectly given in bibliography A, references 106, 107 and 356.
J. T. Randall

Volumetric Analysis. *By G. Fowles. 20 × 13 cm; pp. xii + 202. London: G. Bell and Sons, 1932. Price: six shillings.* This textbook of Volumetric Analysis is written for students and teachers who are concerned with any examination from the School Certificate to the University Honours Degree. It presents therefore an elementary survey of the subject from a theoretical and practical standpoint, and then proceeds to deal in an excellent way with both the older methods of analysis and most of the recent methods that have been thoroughly tested. It contains sections on such physico-chemical principles as are involved in the theory of indicators, oxidation and reduction methods and precipitation processes. The advanced section of this book presents in an admirable way all the volumetric methods which a student would be required to know for an Honours Chemistry Examination, the author evidently having carefully performed the estimations himself. This book, as the author intends, would certainly lead to many of the older processes being superseded by more accurate and frequently also more rapid methods. Adsorption indicators, titanium reduction processes, and the use of liquid amalgams for the reduction of compounds of certain metals are some of the modern improvements dealt with. Some examples of the use of ceric sulphate might usefully have been included.

This book can be recommended confidently to schools, and students brought up on it would find it an admirable textbook even beyond their Honours stage. On the other hand, in the opinion of the reviewer, other textbooks, including both volumetric and gravimetric analysis and excluding the elementary teaching contained in the earlier part of this book would be preferred as a University textbook for a student reading for an Honours degree in Chemistry.
D. C. Jones

Gmelins Handbuch der anorganischen Chemie. *Edited by R. J. Meyer. System-number 59, Section B, Part 5. Eisen. Eighth edition. 25 × 17 cm; pp. 873-1165. Berlin: Verlag Chemie, 1932. Price: 53 marks (subscription price 47.50 marks).* The issue of part 5 completes section B of the chemistry of iron, i.e. the portion dealing with its compounds, and a title page and detailed list of contents accompanies the part. The ferricyanides and ferrocyanides of various metals, the ferrites and ferrates, double chlorides and sulphates, are included in this part. The treatment is comprehensive and modern work appears to be fully covered. Numerous tables and phase rule diagrams are included. The five parts of number 59 of the new Gmelin give the most complete account of the chemistry of iron compounds in existence.
J. R. Partington

Gmelins Handbuch der anorganischen Chemie. *Edited by R. J. Meyer. System-number 58, Section A, Part 2. Kobalt. Eighth edition. 25 × 17 cm; pp. 221-502. Berlin: Verlag Chemie, 1932. Price: 48 marks (subscription price 42 marks).* The issue of this part completes the chemistry of cobalt in the new Gmelin and deals with the compounds of that element. Although many complex compounds, such as cobaltic cyanides, are dealt with, the cobaltammines are not included. There is a section on the colour and constitution of cobalt salts. The treatment, as was to be expected, is very detailed yet concise and the two parts of number 58 form a comprehensive survey of the chemistry of cobalt.
J. R. Partington

Die Valenzzahl und ihre Beziehungen zum Bau der Atome. *By H. Lessheim and R. Samuel. (Fortschritte der Chemie, Physik und physikalischen Chemie). Vol. XIX, No. 3. 24 × 16 cm; pp. 98. Berlin: Gebrüder Borntraeger, 1927. Price: 6.40 marks.* This small monograph gives a general and elementary account of atomic structure from the point of view of Bohr's theory; of the construction of the Periodic System in terms of atomic structure; of the types of valency; of the interpretation of spectra; and of the chemical properties of the atoms as a consequence of their constitution. The part dealing with quantum numbers, which is based on Pauli's principle, is very clear and could usefully supplement any works on the electronic theory of valency which are deficient in this respect.

J. R. Partington

Protoplasmic Action and Nervous Action. *By Ralph S. Lillie. Second edition. 19 × 14 cm, pp. ix + 417. Chicago: The University of Chicago Press, 1932. Price: $3.00.* The first edition appeared in 1923 and was reviewed (**28**, 1001 (1924)). "In this edition some additional references, chiefly to recent books and articles of comprehensive or summarizing nature, have been added at the ends of the chapters. Certain changes in theory or interpretation made necessary by the progress of research, are also briefly indicated." In other words the book is essentially of 1923 and not of 1932. That is a pity because what was good then is not good now.

There is nothing to show, for instance, that Claude Bernard's theory of narcosis is the only one possible now. This is the more remarkable because the author came very close to formulating it himself in 1923.

"Certain definite changes in the physical properties of protoplasm, analogous in many respects with those produced by salts, have been observed in various cases to accompany the action of narcotizing compounds; these changes indicate that underlying narcosis there are definite modifications of the structural conditions in protoplasm; and presumably it is to such modifications that the changes in physiological properties and activity are to be referred," p. 206.

"During narcosis there appears very generally to be a decrease of permeability, an increase in the resistance to structural breakdown or cytolysis, and an increase of protoplasmic viscosity. From the general nature of these changes it would seem that the structural substratum of the living matter assumes temporarily a denser or physically more stable condition," p. 207.

This would have led to reversible agglomeration of living tissue and all its attendant consequences long before the reviewer got into the game if the author had had the courage to think things through. Unfortunately, he followed the line of least resistance.

Warburg and Wiesel also noted "that all of these compounds [alcohols, urethanes, ketones] in sufficient concentration caused precipitation in the press-juice [of yeast], and that the orders of relative precipitating effectiveness and anticatalytic action were the same; this order is also that of relative narcotic action. This parallelism between precipitating action and narcotic action recalls Claude Bernard's hypothesis that a partial coagulation of protoplasmic constituents [proteins] is the essential condition of narcosis. With the living cell, however, much lower concentrations are required to stop fermentation than with the enzyme solution, so that the parallel between the inactivation of the structureless enzyme solution and the inhibition of fermentation in the living cell is not complete. This difference may indicate the importance of the vital organization as such, or it may depend on the presence of special compounds (lipoids) in the living cell," p. 227.

Wilder D. Bancroft

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